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<b>(21) International Application Number:</b> PCT/BE98/00159 <b>(22) International Filing Date:</b> 22 October 1998 (22.10.98)  <b>(30) Priority Data:</b> <table border="0"><tr><td>60/063,487</td><td>22 October 1997 (22.10.97)</td><td>US</td></tr><tr><td>60/074,524</td><td>12 February 1998 (12.02.98)</td><td>US</td></tr><tr><td>98870111.6</td><td>18 May 1998 (18.05.98)</td><td>EP</td></tr></table> <b>(71) Applicant (for all designated States except US):</b> INTERUNIVERSITAIR MICRO-ELEKTRONICA CENTRUM [BE/BE]; Vereniging Zonder Winstbejag, Kapeldreef 75, B-3001 Heverlee (BE).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> VANHAELEMEERSCH, Serge [BE/BE]; Kapelberg 56, B-3001 Leuven (BE). RO-DIONOVICH BAKLANOV, Mikhail [RU/BE]; R. Vander-vaerenlaan 16/8, B-3000 Leuven (BE).  <b>(74) Agents:</b> VAN MALDEREN, Joëlle et al.; Office Van Malderen, Place Reine Fabiola 6/1, B-1083 Brussels (BE).		60/063,487	22 October 1997 (22.10.97)	US	60/074,524	12 February 1998 (12.02.98)	US	98870111.6	18 May 1998 (18.05.98)	EP	<b>(81) Designated States:</b> JP, US, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
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<b>(54) Title:</b> ANISOTROPIC ETCHING OF ORGANIC-CONTAINING INSULATING LAYERS											
<b>(57) Abstract</b> <p>A method for anisotropic plasma etching of organic-containing insulating layers is disclosed. According to this method at least one opening is created in an organic-containing insulating layer formed on a substrate. These openings are created substantially without depositing etch residues by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture which is composed such that the plasma etching is highly anisotropic. Examples of such gaseous mixtures are a gaseous mixture comprising a fluorine-containing gas and an inert gas, or a gaseous mixture comprising an oxygen-containing gas and an inert gas, or a gaseous mixture comprising HBr and an additive. The plasma etching of the organic-containing insulating layer can be performed using a patterned bilayer as an etch mask, said bilayer comprising a hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said hard mask layer.</p>											



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## ANISOTROPIC ETCHING OF ORGANIC-CONTAINING INSULATING LAYERS

### FIELD OF THE INVENTION

5 The present invention is related to the process of semiconductor device fabrication. More in particular, methods including tools and chemistries for anisotropic dry etching of low k polymers are disclosed. These etching processes can be used for definition of via holes and trenches in different interconnect architectures.

### 10 BACKGROUND OF THE INVENTION

The ongoing focus on miniaturisation and the increasing complexity and speed requirements of integrated circuits demand for a continuous higher density integration. To achieve this, there is an ongoing downscaling of the dimensions of the active devices as well as of the structures interconnecting these devices. These interconnect structures can 15 comprise multiple metal levels which are, dependent on the aimed interconnect pattern, either separated one from another by means of interlevel insulating layers or connected one to the other by means of a conductive connection through the insulating layer. Intra-level insulating layers are used to provide isolation within a metal level. Besides this downscaling of the dimensions, additional measures are required to be able to meet the stringent speed 20 specifications like e.g. the signal delay. Conventionally the metal levels are Aluminum layers while the insulating layers are oxide layers. In order to reduce the signal delay one can choose a metal layer with a higher conductivity compared to Aluminum, e.g. a Cu-containing metal layer, and/or choose insulating layers with a lower dielectric constant 25 compared to oxide layers.

This demand for insulating layers with a low dielectric constant has lead to an intensified search for new low K materials to be used as insulating layers. A low  $\epsilon$  material, a low K material and a material with a low permittivity are all alternative 30 expressions for a material with a low dielectric constant, at least for the purposes of this disclosure. The most desirable material should have a low K value, low mechanical stress, high thermal stability and low moisture absorption. Furthermore, the desired material should be selected based on the compatibility with state-of-the-art semiconductor processing steps and tools. Among these new materials are the organic spin-on materials, having a K 35 value in the range from 2.5 to 3, the porous polymers, and the inorganic low-K materials as e.g. xerogels having a K value typically lower than 1.5. The organic materials are of



particular interest because they feature simplified processing, excellent gap-fill and planarization.

Nowadays, there are two major ways of fabricating interconnect structures. In the conventional way as a start a conductive layer, e.g. a metal layer, is formed on an insulating layer (or on the substrate) and patterned thereafter usually by means of reactive ion etching (RIE). Another way is the damascene technology. In the damascene technology, first an insulating layer is deposited and patterned and thereafter a metal layer is deposited to fill the openings, eventually followed by a planarization step to remove the metal excess. The damascene technology has the additional advantage that the difficult metal RIE step is avoided. Damascene processing reduces the problem to dry etching of an insulating layer or a stack of insulating layers. This technique allows to build up horizontal metal patterns as well as vertical metal connections in the surrounding insulating layers. These vertical metal connections are required in order to be able to provide a conductive connection between two horizontal metal patterns being processed in different metal levels. To provide such a connection, usually first openings have to be formed in the insulating layer or in the stack of insulating layers between two different metal levels and filled thereafter with a conductive material. Examples of such openings are via holes or contact holes or trenches. To meet the high density integration requirements, the diameter of these openings is continuously decreasing, while at the same time the aspect ratio of these openings is increasing. Due to the small diameter and the high aspect ratios, the creation of these openings, especially the lithographic steps and the etchings steps involved, is a critical process. Therefore, etching of polymers used as insulating layers requires highly anisotropic etching capabilities.

US patent 5,269,879 is related to the etching of silicon oxide, silicon nitride or oxynitride layers in order to create a via hole extending through such a layer to an underlying electrically conductive layer. Particularly plasma etching is disclosed in an ambient including a fluorine-containing gas, a small amount of a passivating gas, i.e. nitrogen, and eventually an inert gas. This passivating gas is added to the plasma to prevent the sputtering of the underlying electrically conductive layer.

US patent 5,176,790 is related to the etching of mainly silicon oxide, silicon nitride or oxynitride layers in order to create a via hole extending through such a layer to an underlying electrically conductive layer. Particularly plasma etching is disclosed in an ambient including a fluorine-containing gas, a nitrogen-containing gas, and eventually an inert gas. This nitrogen-containing gas is added to the plasma to prevent the sputtering of





the underlying electrically conductive layer. However the amount of nitrogen-containing gas in the ambient is limited. This amount ranges from 1 volume part of nitrogen-containing gas per 2 volume parts of fluorine-containing gas to 1 volume part of nitrogen-containing gas per 15 volume parts of fluorine-containing gas.



## SUMMARY OF THE INVENTION

Etching of insulating layers in semiconductor processing requires highly anisotropic etching capabilities in order to be able to create sub 0.5  $\mu\text{m}$  openings such as via holes, trenches and contact holes. A method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. Preferably, this organic-containing insulating layer comprises at least one unsaturated carbon bond. Examples of organic-containing insulating layer comprising at least one unsaturated carbon bond are organic-containing insulating layers comprising at least one phenyl group. Typical examples are the benzocyclobutarenes, poly arylene ether, aromatic hydrocarbon, and polyimides. These openings are created substantially without depositing etch residues on the exposed layers by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a fluorine-containing gas and an inert gas. Substantially without etch residues means that a limited amount of etch residues can be formed on the exposed layers but that their composition is such that they can easily be removed selective to the organic-containing insulating layer after the openings have been created in subsequent etch or cleaning steps and that they do not affect the anisotropy of the plasma etching. While the plasma etching proceeds, the process conditions are such that the side walls of the openings are fluorinated which advantageously affects the anisotropy of said plasma etching. To obtain anisotropic plasma etching, preferably the spontaneous etching is negligible, while the etch reaction is effectively stimulated by ion bombardment. In other words, the lateral etch rate should be negligible small compared to the vertical etch rate. Particularly by exposing the side walls of the openings to the fluorine-containing gaseous mixture, the chemical composition of the organic-containing insulating layer at the side walls of the openings is modified. This modification results in an increase of the chemical resistance of the fluorinated part of the organic-containing insulating layer, i.e. at the side walls of the openings thereby enhancing the anisotropy of the plasma etching. Plasma etching includes plasma-assisted dry etching as well as reactive ion etching (RIE). The plasma etching of the organic-containing insulating layer can be performed using a patterned bilayer as an etch mask, said bilayer comprising a resist hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said resist hard mask layer. Particularly, said resist hard mask layer is a silicon oxide, or a silicon nitride, or a silicon oxynitride layer, or a silicon carbide layer, or a silicon oxycarbide layer. For the purpose of this disclosure a resist hard mask layer is a layer being used as an etch mask layer or an etch stop layer to selectively remove a resist layer. The plasma etching is preferably but not necessarily selective to said resist hard mask layer. The process conditions are such that a highly anisotropic plasma etch is performed



featuring substantially no undercut of the hard mask layer and substantially with the conservation of the original hard mask profile.

5 In an embodiment of the invention, the openings created in the organic-containing insulating layers comprise at least one via hole, said via hole extending through said insulating layer to an underlying conductive layer or a barrier layer. The plasma etching method of the present invention is selective to this underlying layer. In other words excess removal of this underlying layer is prevented. This underlying conductive and/or barrier layer can be a layer of Ti, TiN, Ta, TaN, Co, silicon nitride, silicon carbide, silicon  
10 oxycarbide, Pt, W, Al, Cu or an alloy of Al or Cu, or any other low resistivity material.

In another embodiment of the invention, the plasma etching method removes the resist layer during the creation of the openings in the organic-containing insulating layers. However in this case, the resist hard mask layer has to be a hard mask layer. For the  
15 purpose of this disclosure, a hard mask layer is defined as a layer which can be etched selective to the underlying layer, i.e. the organic-containing insulating layer. By doing so, a resist strip after the openings have been created is avoided. Therefore the thickness of the resist layer has to be chosen in accordance with the precise etch conditions and the thickness of the insulating layer. Particularly, this is important when the organic containing  
20 insulating layers are silicon-free layers because these silicon-free layers are very sensitive for subsequent etch steps or cleaning steps.

Yet in another embodiment of the invention, the plasma etching method only partly removes the resist layer during the creation of the openings in the organic-containing  
25 insulating layers. The thickness of the resist layer is chosen in accordance with the precise etch conditions and the thickness of the organic-containing insulating layer and such that there is still some resist left-over when the openings are created. Afterwards the resist left-over is removed e.g. using a solvent stripper, or an oxygen-containing plasma, or a combination thereof. Particularly this oxygen-containing plasma can be an oxygen plasma.  
30 This resist removal can be done substantially without consequences for the side walls of the organic-containing insulating layer at the openings provided that said polymer layer is not too sensitive for said oxygen-containing plasma. A typical example of such a layer which is not too sensitive for an oxygen-containing plasma is a layer selected from the group of the benzocyclobutenes.  
35

In a further embodiment of the invention, the gaseous mixture in the reaction chamber further comprises an oxygen-containing gas. Examples of such an oxygen-



containing gas are O<sub>2</sub>, CO, CO<sub>2</sub> and SO<sub>2</sub>, but the invention is not limited hereto. By the addition of a small amount of oxygen to the gaseous mixture, the etch rate is increased.

5 In still a further embodiment of the invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created substantially without depositing etch residues by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a fluorine-containing gas. So no inert gas is present in said gaseous mixture.

10 In a second aspect of the present invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a oxygen-containing gas and an inert gas. The ratio between said oxygen-containing gas and said inert gas in said  
15 gaseous mixture is chosen such that the spontaneous etch rate is substantially zero. So the use of fluorine is avoided which can be beneficial for the further processing because amongst others, fluorine is known to stimulate corrosion, e.g. especially for Cu this can be an issue.

20 The plasma etching of the organic-containing insulating layer, according to the present invention, can be performed using a patterned bilayer as an etch mask, said bilayer comprising a hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said hard mask layer. The plasma etching method has a high selectivity to the hard mask layer formed on the polymer layer. The plasma etch  
25 process creates openings in the organic-containing insulating layer and simultaneously selectively removes the resist layer thereby avoiding a resist strip after etching. Preferably, this organic-containing insulating layer is an organic polymer layer with a low K value. Particularly, this organic-containing insulating layer can be a silicon-free polymer layer.

30 In an embodiment of the invention the oxygen-containing gas in the gaseous mixture is O<sub>2</sub> and the inert gas in the gaseous mixture is nitrogen. The ratio of the amount of nitrogen in said gaseous mixture to the amount of oxygen in said gaseous mixture is preferably in the range from about 10:1 to about 2:1, or from about 30:1 to about 1:1, or from about 50:1 to about 1:1.

35 In another embodiment of the invention a two-step anisotropic etch process is disclosed, wherein in a first step a first part of an opening is created by means of





anisotropic plasma etching using a gaseous mixture comprising a fluorine-containing gas and an inert gas, while in a second step the second part of said opening is etched by means of anisotropic plasma etching using a gaseous mixture comprising an oxygen-containing gas and an inert gas to thereby complete said opening and simultaneously selectively remove the resist.

In a third aspect of the present invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising HBr and an additive, said additive passivating the exposed parts of the insulating layer, i.e. the side walls. Typical examples of such an additive are an inert gas, like N<sub>2</sub>, Ar, He, Xe, Krypton or an oxygen-containing gas, like O<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>O, NO<sub>2</sub>, SO<sub>2</sub>, but the invention is not limited hereto. Preferably, this organic-containing insulating layer is an organic polymer layer with a low K value.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 represents afterglow etch rates of planar SiLK (2) and BCB (1) layers for different NF<sub>3</sub>/O<sub>2</sub> flow ratios.

Figure 2 represents, according to an embodiment of the invention, the etch rate of BCB (Cyclotene 5021<sup>TM</sup>) in a plasma ambient comprising a mixture of NF<sub>3</sub>, O<sub>2</sub> and He versus the percentage of NF<sub>3</sub>. The total gas flow was 115 sccm, whereas the pressure in the chamber was 1.30 Torr. The He flow was kept constant and equal to 65 sccm. The flows of NF<sub>3</sub> and O<sub>2</sub> were chosen complementary and were varied between 0 and 50 sccm, whereby the sum of the NF<sub>3</sub> flow and the O<sub>2</sub> flow was kept constant and equal to 50 sccm. The percentage of NF<sub>3</sub> in the figure is the relative amount of NF<sub>3</sub> compared to the amount of NF<sub>3</sub> and O<sub>2</sub> without taking into account He.

Figure 3 represents the change in refractive index of SiLK and BCB as a function of etch time in a NF<sub>3</sub> afterglow plasma.

Figure 4 represents etch rates of SiLK and BCB in RIE conditions with changing SF<sub>6</sub>/O<sub>2</sub> gas flow ratios (0 = pure O<sub>2</sub> diluted in N<sub>2</sub>, 100 = pure SF<sub>6</sub> diluted in N<sub>2</sub>).



Figure 5 represents a SEM picture of the via holes in an organic-containing insulating layer (7), i.e. a BCB layer, after plasma etching according to an embodiment of the invention in an ambient comprising  $\text{SF}_6$  and  $\text{N}_2$ . The picture shows a  $\text{SiO}_2$  layer (8), remaining resist (9), intact Ti/TiN barrier layer (6) on a conductive AlSiCu layer (5). Layer (4) is again a Ti/TiN barrier layer. No undercut of the  $\text{SiO}_2$  layer can be detected.

Figure 6 represents a SEM picture of via holes in an organic-containing insulating layer (7), i.e. a SILK layer, after plasma etching according to an embodiment of the invention in an ambient comprising  $\text{O}_2$  and  $\text{N}_2$ , showing intact  $\text{SiO}_2$  layer (8), intact Ti/TiN barrier layer (6) on a conductive AlSiCu layer (5). No undercut of the  $\text{SiO}_2$  layer can be detected.

Figure 7 represents a SEM picture of trenches in an organic-containing insulating layer (7), i.e. a SILK layer, after plasma etching according to an embodiment of the invention in an ambient comprising  $\text{N}_2$  and  $\text{O}_2$  at a ratio of 5:1, showing intact  $\text{SiO}_2$  layer (8). No undercut of the  $\text{SiO}_2$  layer can be detected.

Figure 8 represents, according to an embodiment of the invention, a detailed description of the processing steps involved to create a particular interconnect structure, i.e. a dual-damascene structure.

Figure 9 represents a SEM picture of trenches in an organic-containing insulating layer (7), i.e. a SILK layer, after a two-step plasma etching according to an embodiment of the invention, showing intact  $\text{SiO}_2$  layer (8). No undercut of the  $\text{SiO}_2$  layer can be detected.



## DETAILED DESCRIPTION OF THE INVENTION

In relation to the appended drawings the present invention is described in detail in the sequel. It is apparent however that a person skilled in the art can imagine several other equivalent embodiments or other ways of executing the present invention, the spirit and scope of the present invention being limited only by the terms of the appended claims.

In a first aspect of the present invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created substantially without depositing etch residues by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a fluorine-containing gas and an inert gas. Preferably, this organic-containing insulating layer comprises at least one unsaturated carbon bond. Examples of organic-containing insulating layer comprising at least one unsaturated carbon bond are organic-containing insulating layers comprising at least one phenyl group. Typical examples are the benzocyclobutrenes, e.g. Cyclotene 5021<sup>TM</sup> from Dow Chemical with chemical formulation divinyl siloxane benzocyclobutane (BCB), poly arylene ether, e.g. FLARE<sup>TM</sup> II, aromatic hydrocarbon, e.g. SILK<sup>TM</sup>. The substrate can be a partly processed or a pristine wafer or slice of a semi-conductive material, like Si or Ga As or Ge, or an insulating material, e.g. a glass slice, or a conductive material. Said substrate can comprise a patterned conductive layer. Particularly, in case said substrate is a partly processed wafer or slice; at least a part of the active and/or passive devices can already be formed and/or at least a part of the structures interconnecting these devices can be formed.

To obtain anisotropic plasma etching, preferably the spontaneous etching is limited or negligible, while the etch reaction is effectively stimulated by ion bombardment. In other words, the lateral etch rate should be negligible small compared to the vertical etch rate. Particularly by exposing the side walls of the openings, i.e. the surface of the organic-containing insulating layer comprising at least one phenyl group at these side walls of these openings, to the fluorine-containing gaseous mixture during the plasma etching, these side walls are fluorinated which advantageously affects the anisotropy of said plasma etching. By doing so, the chemical composition of the organic-containing insulating layer comprising at least one unsaturated carbon bond is modified at the side walls of the openings. Particularly, organic-containing insulating layers comprising phenyl groups contain such unsaturated carbon bonds. These carbon bonds, which can be attacked by reactive species such as atomic fluorine generated in a plasma or another ambient comprising active fluorine. Said active fluorine can abstract hydrogen from carbon in said



phenyl groups. Therefore, the method involves a formal replacement of hydrogen by fluorine. Furthermore, due to the small size of the fluorine atoms, they can easily diffuse through the insulating layer. Consequently the replacement of hydrogen by fluorine is not limited to the surface of the layer but can extend also further in the layer. Fluorine is the most electronegative and the least polarizable element on the periodic table. The incorporation of fluorine in the insulating layer at the side walls of the openings makes the fluorinated part of the insulating layer less polarizable leading to an increase in chemical resistance and a decrease of the K value of said part, said part starts at a surface and extends in the insulating layer with elapsing exposure time. So particularly, this in-situ fluorination results in an increase of the chemical resistance of the fluorinated part of the organic-containing insulating layer, i.e. at the side walls of the openings thereby enhancing the anisotropy of the plasma etching. It should be clear however that during the plasma etching the bottom side of the openings, i.e. a surface of the insulating layer at the etch front of the opening is also exposed to the gaseous mixture comprising fluorine. But contrary to the side walls, at the bottom side of the openings fluorination is prevented or at least the effect of the fluorination is nullified by the ion bombardment. Plasma etching includes plasma-assisted dry etching as well as reactive ion etching (RIE). The plasma etching of the organic-containing insulating layer can be performed using a patterned bilayer as an etch mask, said bilayer comprising a resist hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said hard mask layer. Particularly, said resist hard mask layer can be a silicon oxide, or a silicon nitride, or a silicon oxynitride, or a silicon carbide, or a silicon oxycarbide. By doing so a highly anisotropic plasma etch is performed featuring substantially no undercut of the resist hard mask layer and with the conservation of the original resist hard mask profile.

The pressure in the reaction chamber is typically between 1 mTorr and 100 mTorr, or between 1 mTorr and 300 mTorr, or between 1 mTorr and 5 Torr. The setting temperature is typically between -10 °C and 50 °C, -30 °C and 50 °C, or -60 °C and 70 °C. This setting temperature is the temperature as set on the heating/cooling source. The actual temperature in the reaction chamber can be higher dependent on the plasma conditions. Typical examples of fluorine-containing gases are SF<sub>6</sub>, or NF<sub>3</sub>, or C<sub>2</sub>F<sub>6</sub>, or CF<sub>4</sub> or CHF<sub>3</sub> or CH<sub>3</sub>F or CH<sub>2</sub>F<sub>2</sub> or mixtures thereof. The inert gas can be helium or argon or krypton or nitrogen or xenon or krypton. The inert gas is preferably nitrogen. More preferably, the ratio of the amount of nitrogen in said gaseous mixture to the amount of fluorine-containing gas in said gaseous mixture is larger than 2:1.





In case the opening is a via hole, the plasma etching is performed until the surface of an underlying conductive layer or an underlying barrier layer is reached while preventing excess removal of the underlying layer. This underlying conductive and/or barrier layer can be a layer of Ti, TiN, Ta, TaN, Co, silicon nitride, silicon carbide, silicon oxycarbide, Pt, W, Al, Cu or an alloy of Al or Cu, or any other low resistivity material.

As an example, an anisotropic plasma etch process to create openings in a BCB layer is disclosed.

Experimental conditions are:

etch tool : high density plasma reactor (TCP 9400)

gaseous mixture for the plasma etch : SF<sub>6</sub> and N<sub>2</sub>

etch conditions in chamber: 15 mTorr

TCP power : 700 watt

bottom power : 100 watt

hard mask layer is a PECVD oxide layer with a thickness of 250 nm

thickness of the resist layer (Sumitomo I-line resist): 1.2  $\mu$ m

thickness of BCB layer: 0.7  $\mu$ m

underlying layer: TiN layer

set-point temperature : 20 °C

Under these conditions the BCB layer was etched with an etch rate of 500 nm/min, yielding a highly anisotropic etch profile and substantially no hard mask undercut (figure 5). Furthermore the resist hard mask profile was kept intact and there was substantially no TiN loss. When reaching the surface of the TiN layer the thickness of the remaining resist left-overs was about 0.1  $\mu$ m. These resist left-overs can be removed by a subsequent etching step without attacking the other materials present on the wafer, particularly the BCB. Then, eventually, a cleaning step can be performed using diluted H<sub>2</sub>SO<sub>4</sub> to remove the residues without attacking the other materials present on the wafer. Alternatively, instead of H<sub>2</sub>SO<sub>4</sub> EKC 265 or a combination of H<sub>2</sub>SO<sub>4</sub> and EKC 265 can be used.

With this etch chemistry, resist hard mask undercut is prevented due to the fluorination of at least a part of the BCB layer. This fluorination is obtained by exposure of the side walls of the BCB layer to an ambient comprising fluorine. Said fluorination increases the chemical and mechanical resistance of said BCB as clearly supported by figures 1, 2 and 3.



Figure 1 shows the etch rate of a planar BCB layer (1) and a SILK layer (2) under afterglow conditions, i.e. without ion bombardment, in a gaseous mixture comprising a fluorine-containing gas, being  $\text{NF}_3$ , and an oxygen-containing gas, being  $\text{O}_2$ . It is observed that the etch rate in pure fluorine-containing plasma is substantially zero. It is also observed that this exposure affects only a part of the layer, said part starting at the exposed surface of the layer and extending into the layer. The thickness of said fluorinated part of the film depends on the atomic fluorine concentration, the fluorination time, i.e. the exposure time, and the temperature. This observation confirms the expectations because the fluorination is a diffusion limited process. The fluorination of said part of the BCB layer, leads to a change of refractive index and chemical composition of said fluorinated part of the BCB layer. This is also observed for SILK films and Flare-II films. As depicted in Fig. 2, the etch rate for etching a fluorinated BCB film (3) in a  $\text{O}_2/\text{NF}_3$  afterglow plasma can be substantially lower than the etch rate for etching pristine BCB films (1), dependent on the  $\text{O}_2/\text{NF}_3$  ratio. The change of the refractive index (figure 3) is also indicative for the fluorination of the BCB layer under pure  $\text{NF}_3$  afterglow conditions. Lowering of the refractive index results in a lowering of the K-value. From these observations in an afterglow plasma, one can conclude that lateral etching in a plasma etch process, e.g. RIE, can be controlled by the choice of the right process chemistry. The vertical etch rate however will be higher in RIE as compared to afterglow because energy is still provided to the surface by means of ion bombardment. The vertical etch rates obtained in RIE for  $\text{SF}_6/\text{N}_2$  chemistries are shown in figure 4. From the figures, one can conclude that working under oxygen free etch conditions allows sufficient etch rate (vertical) with substantially zero etch rate in the lateral direction.

In a second aspect of the present invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a oxygen-containing gas and an inert gas. Preferably, this organic-containing insulating layer is a low K polymer layer. Particularly, this organic-containing insulating layer can be a silicon-free polymer layer. Typical examples are poly arylene ether, i.e. FLARE<sup>TM</sup> II, aromatic hydrocarbon, i.e. SILK<sup>TM</sup>. To obtain anisotropic plasma etching, preferably the spontaneous etching is limited or negligible, while the etch reaction is effectively stimulated by ion bombardment. In other words, the lateral etch rate should be negligible small compared to the vertical etch rate. As can be deduced from fig. 1 the spontaneous etch rate of a planar SILK layer (2) and a planar BCB layer (1) under afterglow conditions, i.e. without ion bombardment, in a pure oxygen ambient is, although, below 100 nm per minute, far too high making such a



pure oxygen ambient unsuited for anisotropic plasma etching. However, by introducing an appropriate amount of an inert gas the spontaneous etching rate can be reduced to substantially zero. The plasma etching of the organic-containing insulating layer, according to the present invention, can be performed using a patterned bilayer as an etch mask, said bilayer comprising a hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said hard mask layer. The plasma etching method has a high selectivity to the hard mask layer formed on the polymer layer. Particularly, said hard mask layer can be a silicon oxide, or a silicon nitride, or a silicon oxynitride, or a silicon carbon, or a silicon oxycarbon layer. The plasma etch process creates openings in the organic-containing insulating layer and simultaneously removes the resist layer thereby avoiding a resist strip after etching. By doing so a highly anisotropic plasma etch is performed featuring substantially no undercut of the hard mask layer, selective to the hard mask layer and with the conservation of the original hard mask profile. Preferably (fig.7), the side walls of the openings are slightly positively sloped yielding a better performance and reliability in the subsequent processing steps, as e.g. filling the opening with a metal.

The pressure in the reaction chamber is typically between 1 mTorr and 100 mTorr, or between 1mTorr and 300 mTorr, or between 1 mTorr and 5 Torr. The setting temperature is typically between -10 °C and 50 °C, -30 °C and 50 °C, or -60 °C and 70 °C. This setting temperature is the temperature as set on the heating/cooling source. The actual temperature in the reaction chamber can be higher dependent on the plasma conditions. Preferably the oxygen-containing gas is O<sub>2</sub> but the invention is not limited hereto. The inert gas can be helium or argon or krypton or xenon or nitrogen. The inert gas is preferably nitrogen. More preferably, the ratio of the amount of nitrogen in said gaseous mixture to the amount of oxygen in said gaseous mixture is in the range from 10:1 to 2:1 or from 30:1 to 1:1.

In case the opening is a via hole, the plasma etching is performed until the surface of the underlying conductive layer or the underlying barrier layer is reached while preventing excess removal of the underlying layer. This underlying conductive and/or barrier layer can be a layer of Ti, TiN, Ta, TaN, Co, silicon nitride, silicon carbide, silicon oxycarbide, Pt, W, Al, Cu or an alloy of Al or Cu, or any other low resistivity material.

In an embodiment of the invention, as an experimental example, an anisotropic etch process on a silicon-free polymer layer, i.e. a SILK layer is disclosed. Experimental conditions are:



etch tool : high density plasma reactor (TCP 9100)  
gaseous mixture for the plasma etch : O<sub>2</sub> and N<sub>2</sub>  
etch conditions in chamber: 5 mTorr  
TCP power : 400 watt  
5 bottom power : 200 watt  
hard mask layer is a PECVD oxide layer with a thickness of 250 nm  
thickness of the resist layer (Sumitomo I-line): 1.2  $\mu$ m  
thickness of SILK layer: 1.1  $\mu$ m  
underlying layer: TiN layer  
10 set-point temperature : 20 °C

Under these conditions the SILK layer was etched with an etch rate of 500 nm/min, yielding via holes (fig. 6) with a highly anisotropic etch profile and substantially no hard mask undercut. Furthermore the hard mask profile was kept intact and there was  
15 substantially no TiN loss. When reaching the surface of the TiN layer the resist layer was totally removed. Then a cleaning step was performed using diluted H<sub>2</sub>SO<sub>4</sub> to remove the residues without attacking the other materials present on the wafer. Alternatively, instead of H<sub>2</sub>SO<sub>4</sub>, EKC 265 or a combination of H<sub>2</sub>SO<sub>4</sub> and EKC 265 or an SPM solution can be used.

20 In another embodiment of the invention, prior to the step of anisotropic plasma etching of an organic-containing insulating layer in an ambient comprising an oxygen-containing gas and an inert gas, a first part of an opening is created in said organic-containing insulating layer by plasma etching in an ambient comprising a fluorine-containing gas and an inert gas. In fact a two-step anisotropic etch process is disclosed (as  
25 in fig.9) wherein in a first step a first part of an opening is created by means of anisotropic plasma etching using a gaseous mixture comprising a fluorine-containing gas and an inert gas, while in a second step the second part of said opening is etched by means of anisotropic plasma etching using a gaseous mixture comprising an oxygen-containing gas  
30 and an inert gas to thereby complete said opening and simultaneously selectively remove the resist. The openings formed by this two-step etch process have slightly positively sloped side walls. As an example (figure 8), a particular dual-damascene structure is described. During the fabrication of such a structure the method of the present invention is utilised. It should be clear however that the invention is not limited to this particular structure but the  
35 present invention can be applied for any isolation or interconnect structure comprising organic-containing insulating layers wherein openings have to be created. According to the example (fig.8):





A first dielectric layer (12), i.e. an organic polymer layer comprising phenyl groups is formed on a substrate (11) comprising a patterned conductive layer (10). Said conductive layer can be a single conductive layer or a combination of a conductive layer and a barrier layer. Examples of such polymers are the benzocyclobutarenes, i.e. benzocyclobutene (BCB) commercially available as Cyclotene 5021<sup>TM</sup>, poly arylene ether, i.e. FLARE<sup>TM</sup> II, aromatic hydrocarbon, i.e. SILK<sup>TM</sup>, polyimides.

A first hard mask layer (13), e.g. a silicon oxide or a silicon nitride or a silicon oxynitride layer or a SiC layer, is formed on this organic polymer film. Then a patterned resist layer (14) is formed thereon (fig.8, step a)). Further, said first hard mask layer is patterned (fig.6, step b)) using said patterned resist layer as a mask and said second resist layer is removed.

A second dielectric layer, i.e. an organic-containing insulating layer comprising at least one phenyl group (15), is formed (step c)) on the patterned first hard mask layer. A patterned bilayer (16) is formed (step d)) on said second dielectric layer. This bilayer comprises a second hard mask layer, being formed on said second dielectric layer, and a second resist layer being formed on said second hard mask layer.

The first and the second dielectric layer can be etched by means of the anisotropic plasma etching method of the present invention. There are at least two possibilities.

As a first possibility, a first part of the openings can be formed by plasma etching said second dielectric layer in a gaseous mixture comprising a fluorine containing gas and an inert gas using the patterned bilayer as an etch mask which can result in the formation of a first part of a trench and a first part of a via hole. In such case, the first hard mask layer not necessarily functions as an etch stop layer. The thickness of the second resist layer is chosen in accordance with the etch time such that when this first timed etch is stopped there is still some resist left and said first hard mask layer is not yet reached. Thereafter the etch in said second dielectric layer is continued by plasma etching in a gaseous mixture comprising an oxygen-containing gas and an inert gas. This second etch is selective to said first and said second hard mask layer thereby preventing the extension from the trench in the first dielectric layer (step e)). The first dielectric layer is then etched in a gaseous mixture comprising an oxygen-containing gas and an inert gas using the patterned first hard mask layer as a mask to form a via hole i.e. exposing the surface of the underlying conductive layer (step e)).

As a second possibility, the openings can be formed by plasma etching said second dielectric layer in a gaseous mixture comprising an oxygen-containing gas and an inert gas using the patterned bilayer as an etch mask. This etch is selective to said first and said second hard mask layer thereby preventing the extension from the trench in the first dielectric layer (step e)). The first dielectric layer is then etched in a gaseous mixture



comprising an oxygen-containing gas and an inert gas using the patterned first hard mask layer as a mask to form a via hole i.e. exposing the surface of the underlying conductive layer (step e)). The etching of the first and second dielectric layer can be performed using a single etch step or two subsequent etch steps.

5 Both possibilities have the common advantage that the second resist layer is completely and selectively removed.

Thereafter said second hard mask layer can be removed (as in fig. 8 step e)) or not.

10 A conductive layer, e.g. an alloy of or pure Al, Cu, Ag, Pt, Co, Ti, Ni or Au, or a combination of a conductive layer (18) and a barrier layer (17), like e.g. a Ti-containing layer or a Co-containing or a Ni-containing layer or a Ta-containing layer, can be deposited (steps f) and g)) thereby filling the via hole in the first and second dielectric layer and the trench in the second dielectric layer.

15 In a third aspect of the present invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising HBr and an additive, said additive passivating the exposed parts of the insulating layer, i.e. the side walls. Typical examples of such an additive are an inert gas, like N<sub>2</sub>, Ar, He, Xe, krypton or an oxygen  
20 containing gas, like O<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>O, NO<sub>2</sub>, SO<sub>2</sub>, but the invention is not limited hereto. In fact, a wide variety of additives can be used for increasing the etch rate and/or for additional side wall passivation possibly resulting in positively sloped profiles. In an embodiment of the invention, said gaseous mixture can further comprise fluorine-containing gases in order to increase the etch rate while keeping the selectivities and profiles  
25 substantially unchanged by balancing the gas flows.

In another embodiment of the invention, said gaseous mixture can further comprise chlorine-containing gases in order to increase the etch rate while keeping the profiles substantially unchanged and allowing a slight decrease of the selectivities by balancing the  
30 gas flows.

The organic-containing insulating layer can be plasma etched using the combination of a patterned hard mask layer and a patterned resist layer as an etch mask by means of plasma etching. The organic-containing insulating layer can be a polymer layer, preferably  
35 having a low permittivity. Particularly also silicon-containing polymer layers can be used. The pressure in the chamber is typically between 1 mTorr and 50 mTorr or between 1 mTorr and 5 Torr.. By doing so a highly anisotropic etch is performed featuring



substantially no undercut of the hard mask layer, selective to the hard mask layer and with the conservation of the original hard mask profile. Furthermore, in case said opening is a via hole, this highly anisotropic etch is selective to the underlying conductive layer or barrier layer.

5

Particularly, towards the silicon-containing polymers, HBr will help in obtaining higher etch rates by generating SiBr etch products which can be volatilized by means of ion bombardment. At the same time, lateral etching will be substantially inhibited by the formation of  $\text{Si}_x\text{Br}_y\text{O}_z$  passivation layers, x, y and z being positive whole numbers.

10

Possibly also C can be incorporated in these passivation layers. These passivation layers are stable as long as there is no exposure to ion bombardment. Particularly, the side walls of the via holes and/or trenches are not exposed to such an ion bombardment. The plasma etch process will have a very high selectivity towards hard mask materials allowing the resist to be removed during the etch process with conservation of the hard mask thickness and profile. As a consequence, this process will allow much thinner hard masks to be used for the formation of via holes and/or trenches. Selectivity both to the hard mask layer and to the underlying conductive layer can be obtained by controlling the ion energy.

15

Towards the silicon-free polymers, this plasma etch process will allow improved profiles because of the limited lateral etch rate. This will allow high over-etch times whenever needed. The plasma etch process will have a very high selectivity towards hard mask materials allowing the resist layer to be removed during the etch process with conservation of the hard mask thickness and profile. As a consequence, this process will allow much thinner hard mask layers to be used for the formation of via holes and/or trenches. Selectivity both to hard mask layer and eventually to the underlying conductive layer can be obtained by controlling the ion energy.

20

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## WHAT IS CLAIMED IS:

1. A method for forming at least one opening in an organic-containing insulating layer, comprising the steps of:
  - 5       creating said opening by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a fluorine-containing gas and an inert gas; and
  - 10       controlling said plasma etching, while creating said opening, in a manner that substantially no etch residues are deposited and that the side walls of said opening are fluorinated during said plasma etching to thereby enhance the anisotropy of said plasma etching.
- 15       2. A method as recited in claim 1, wherein said organic-containing insulating layer comprises at least one unsaturated carbon bond.
- 20       3. A method as recited in claim 2, wherein said organic-containing insulating layer is selected from a group comprising the benzocyclobutarenes, poly arylene ether, aromatic hydrocarbon, and polyimides.
- 25       4. A method as recited in claim 1, wherein said plasma etching is performed using a patterned bilayer as a mask, said bilayer comprising a resist hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said resist hard mask layer.
- 30       5. A method as recited in claim 4, wherein said resist hard mask layer is a silicon oxide, or a silicon nitride, or a silicon oxynitride, or a silicon carbide, or a silicon oxycarbide layer.
- 35       6. A method as recited in claim 1, wherein said inert gas is nitrogen and wherein the ratio of the amount of nitrogen in said gaseous mixture to the amount of fluorine containing gas in said gaseous mixture is larger than 2:1.
7. A method as recited in claim 1, wherein said fluorine-containing gas is  $\text{SF}_6$ , or  $\text{NF}_3$ , or  $\text{C}_2\text{F}_6$ , or  $\text{CF}_4$  or  $\text{CHF}_3$  or  $\text{CH}_3\text{F}$  or  $\text{CH}_2\text{F}_2$  or mixtures thereof.
8. A method as recited in claim 1, wherein said opening is at least one via hole, said via hole extending through said insulating layer to an underlying conductive layer or an underlying barrier layer.





9. A method as recited in claim 1, wherein said gaseous mixture further comprises an oxygen containing gas.

5 10. A method for forming at least one opening in an organic-containing insulating layer comprising the step of:

creating said opening by plasma etching said organic-containing insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising an oxygen-containing gas and an inert gas, said inert gas and said oxygen-containing gas being  
10 present in said gaseous mixture at a predetermined ratio, said ratio being chosen such that spontaneous etching is substantially avoided.

11. A method as recited in claim 10, wherein said organic-containing insulating layer is a low K organic polymer layer.

15 12. A method as recited in claim 10, wherein said plasma etching is performed using a patterned bilayer as a mask, said bilayer comprising a hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said resist hard mask layer.

20 13. A method as recited in claim 12, wherein said resist layer is selectively removed from said hard mask layer while creating said opening.

25 14. A method as recited in claim 10, wherein said oxygen-containing gas in said gaseous mixture is O<sub>2</sub> and said inert gas in said gaseous mixture is nitrogen.

15. A method as recited in claim 14, wherein said ratio of nitrogen in said gaseous mixture to oxygen in said gaseous mixture is in the range from 5:1 to 2:1.

30 16. A method as recited in claim 10, wherein prior to plasma etching in said reaction chamber containing said gaseous mixture, a first part of said opening is created by plasma etching said insulating layer in said reaction chamber containing a first gaseous mixture, said first gaseous mixture comprising a fluorine-containing gas and an inert gas;

controlling said plasma etching in said reaction chamber containing said first  
35 gaseous mixture, while creating said first part of said opening, in a manner that substantially no etch residues are deposited and that the side walls of said first part of said



opening are fluorinated during said plasma etching to thereby enhance the anisotropy of said plasma etching in said reaction chamber containing said first gaseous mixture.

17. A method as recited in claim 16, wherein said opening has positively sloped side walls.



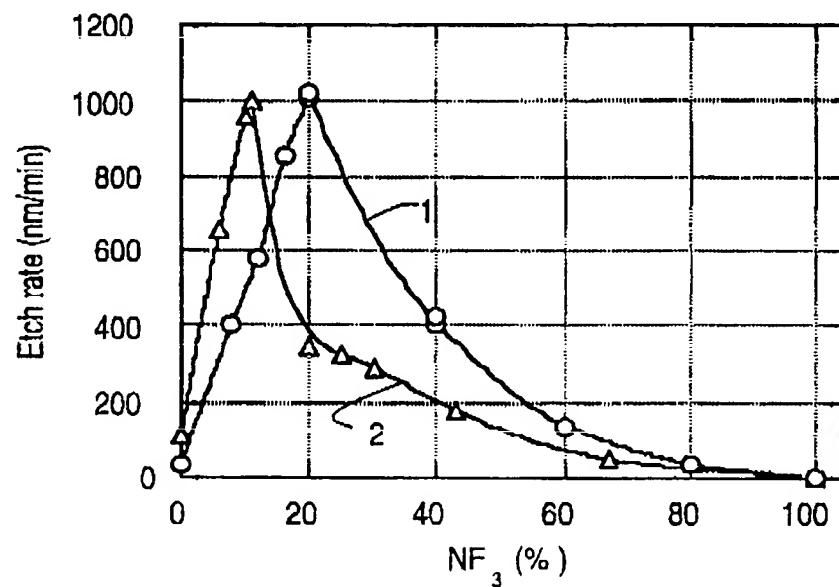
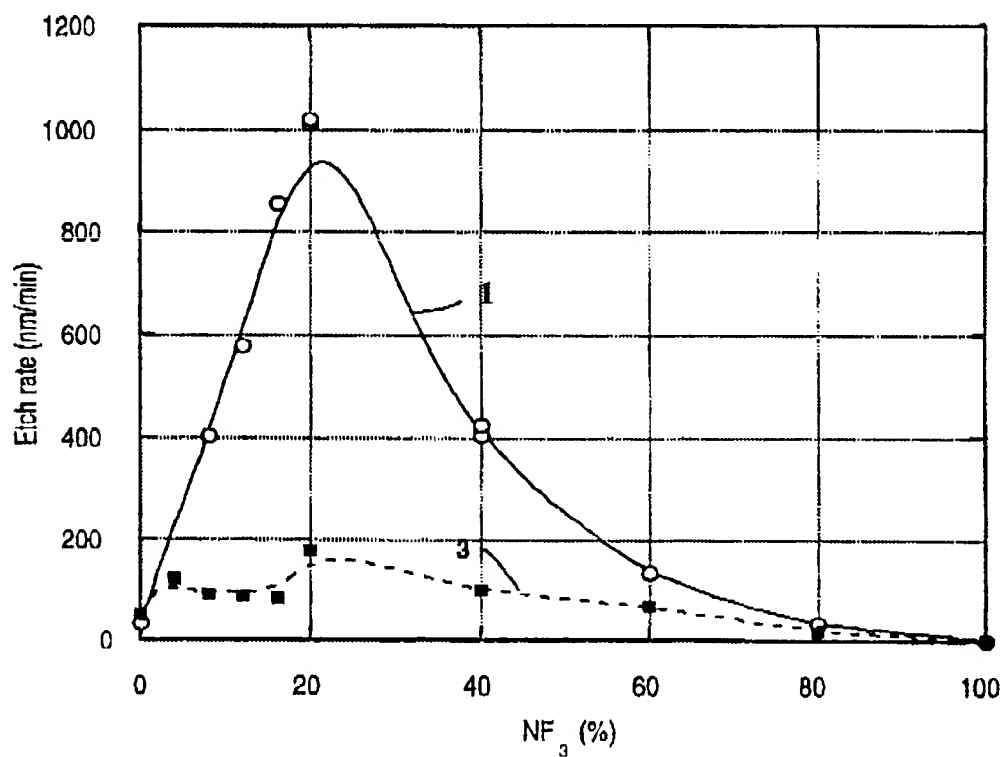
Figure 1Figure 2



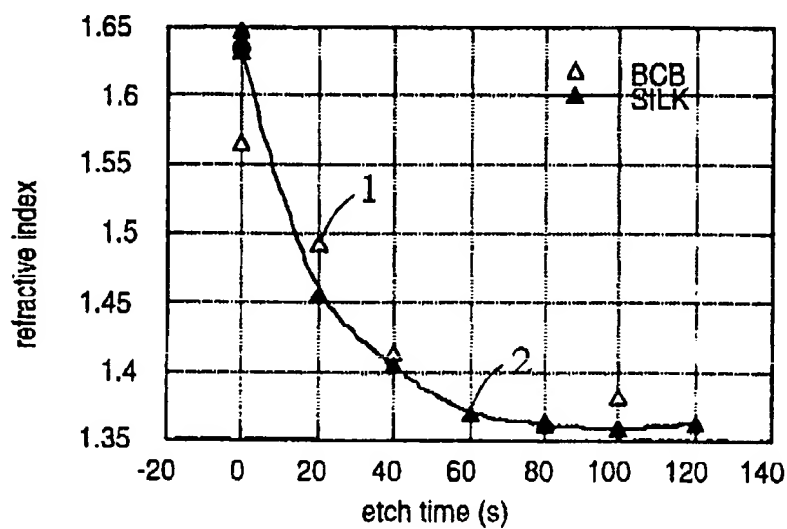
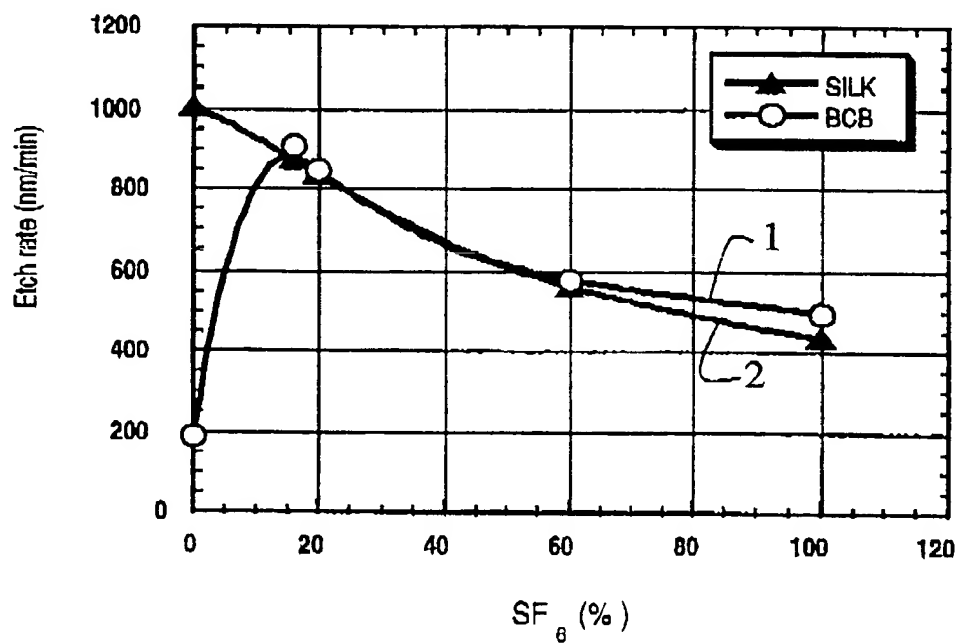
Figure 3Figure 4





Figure 5

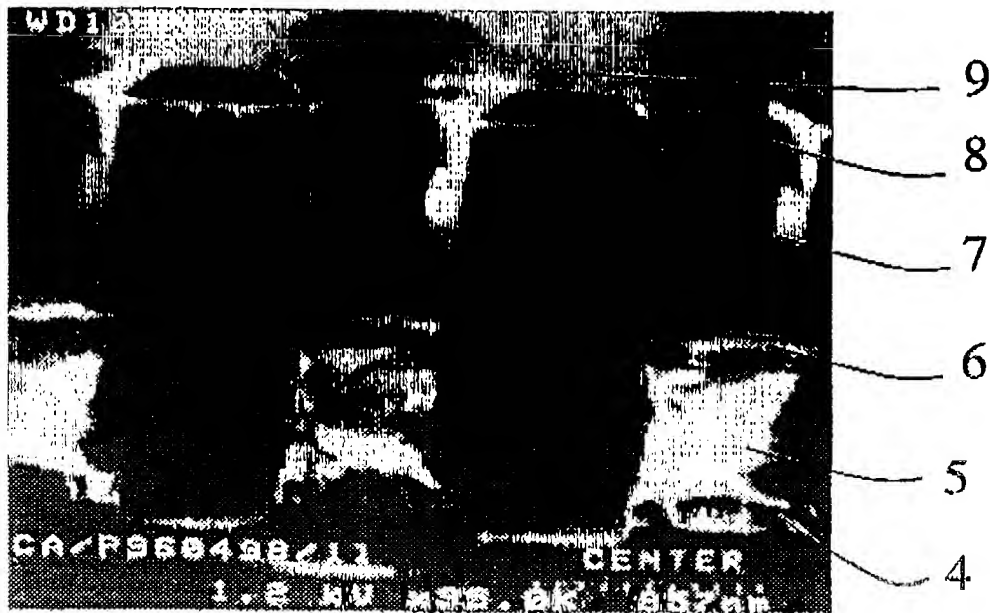


Figure 6

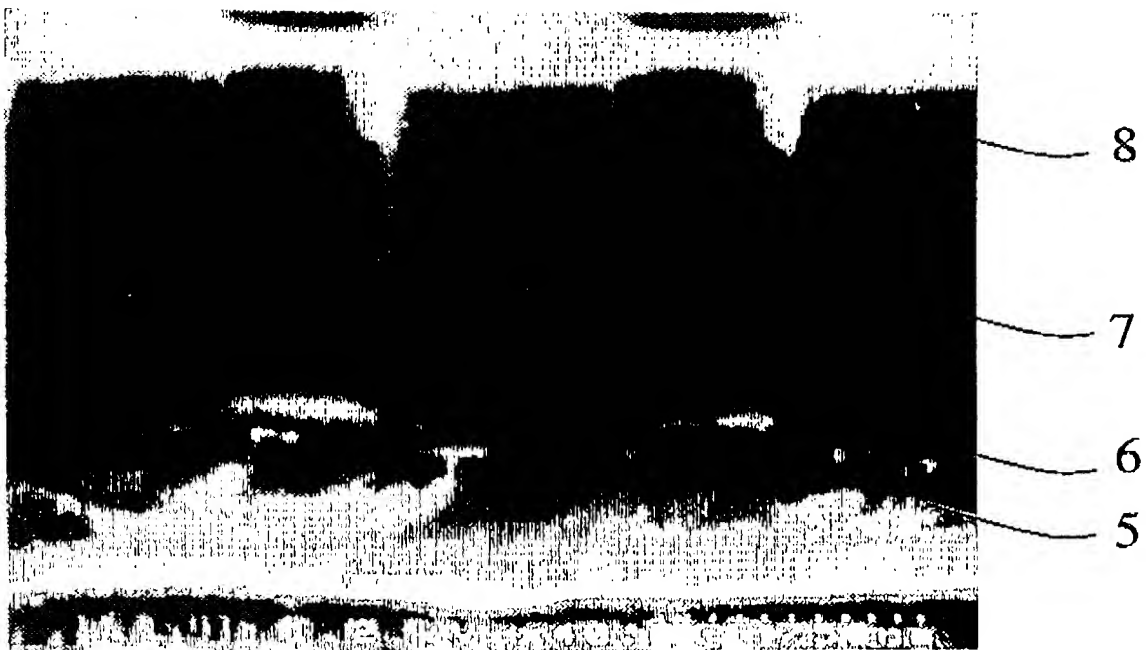




Figure 7

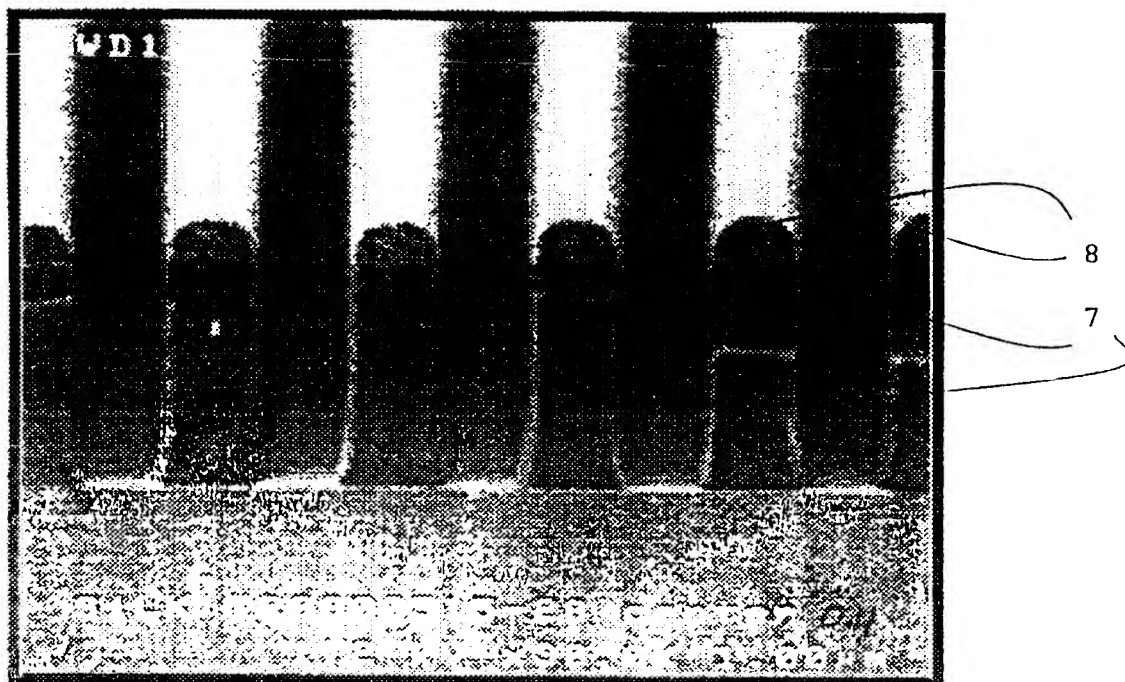




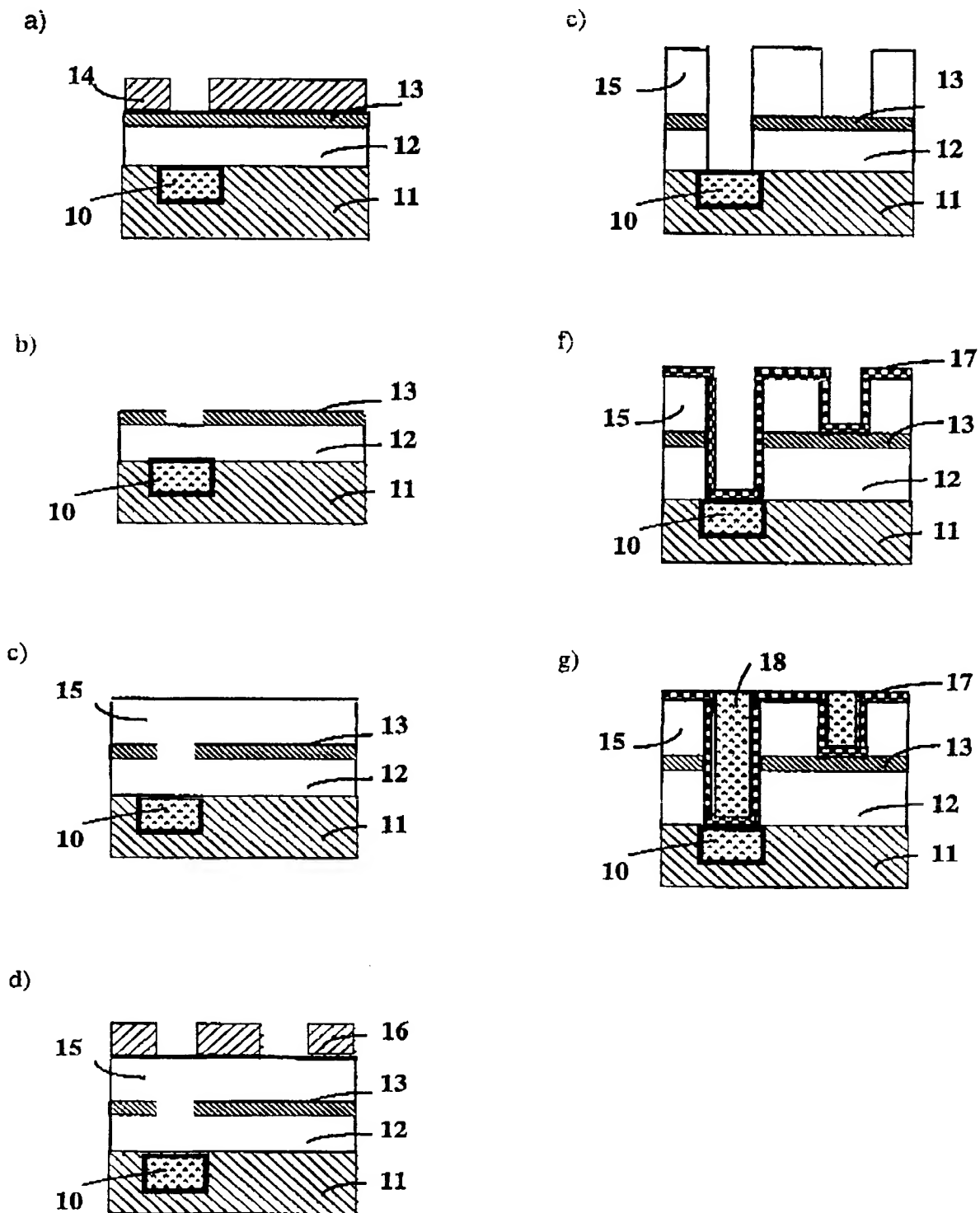
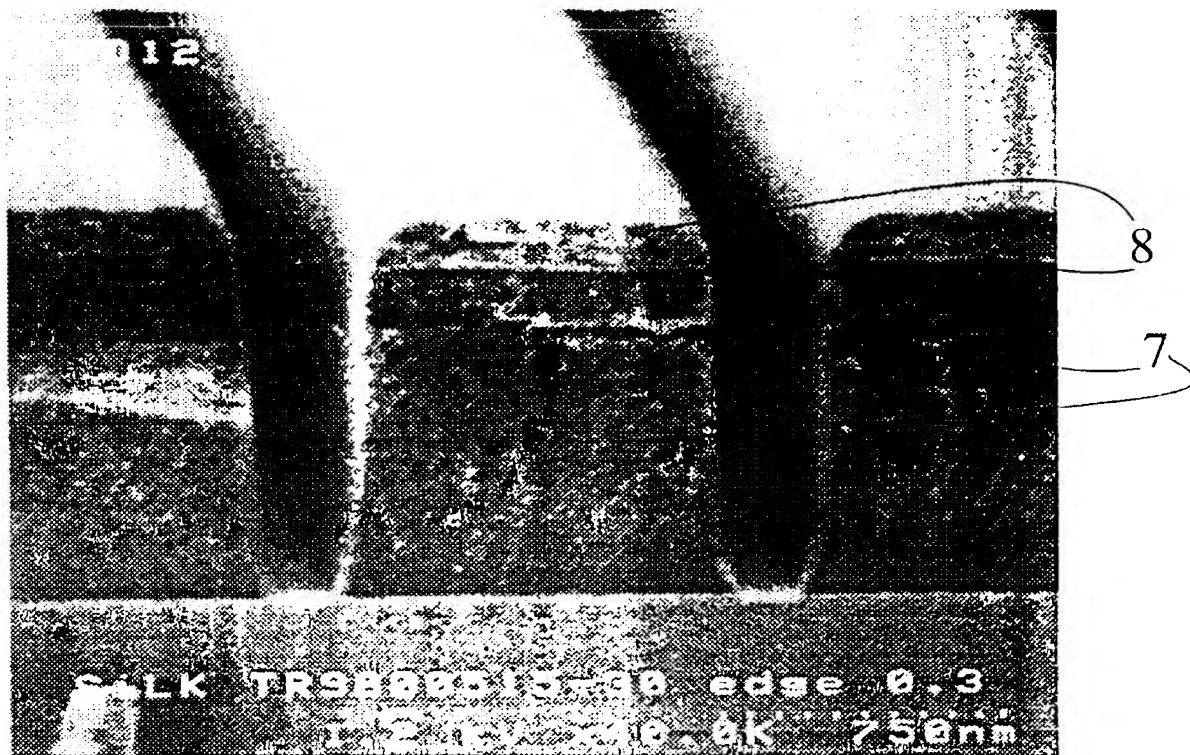
Figure 8



Figure 9







# INTERNATIONAL SEARCH REPORT

International Application No

PCT/BE 98/00159

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 H01L21/3065

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 816 196 A (LA COMBE) 11 June 1974 see Abstract see claims 1,2	1-15
X,P	PATENT ABSTRACTS OF JAPAN vol. 98, no. 5, 30 April 1998 & JP 10 012617 A (MITSUBISHI ELECTRIC CORP.), 16 January 1998 see Abstract	1-15
X	US 5 176 790 A (ARLEO ET AL.) 5 January 1993 cited in the application see claims 1,2,17,26; figures 1,2	1-9
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents

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- "P" document published prior to the international filing date but later than the priority date claimed

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- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

12 February 1999

Date of mailing of the international search report

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# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/BE 98/00159

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 661 204 A (MATHUR ET AL.) 28 April 1987 see Abstract see claims 1,4-6 ---	1-15
X	US 5 173 442 A (CAREY) 22 December 1992 see column 4, line 3-8; claim 1; figures 1A-1F ---	1-15
X	US 5 358 902 A (VERHAAR ET AL.) 25 October 1994 see column 5, line 22-32 see claims 1,2,7 ---	1-15
A	DATABASE WPI Section Ch, Week 9530 Derwent Publications Ltd., London, GB; Class L03, AN 95-230257 XP002093190 & RU 2 024 991 A (MOLECULAR ELECTRON RES. INST.), 15 December 1994 see abstract ---	1-17
A	US 5 269 879 A (RHOADES ET AL. ) 14 December 1993 cited in the application see Abstract ---	1-17
A	EP 0 127 188 A (KK TOSHIBA) 5 December 1994 see claims 9-14 -----	1-17



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/BE 98/00159

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 3816196 A	11-06-1974	NONE	
US 5176790 A	05-01-1993	NONE	
US 4661204 A	28-04-1987	AU 581110 B AU 6549886 A EP 0244462 A JP 63501186 T WO 8702626 A	09-02-1989 19-05-1987 11-11-1987 28-04-1988 07-05-1987
US 5173442 A	22-12-1992	US 5091339 A US 5219787 A	25-02-1992 15-06-1993
US 5358902 A	25-10-1994	GB 2233494 A DE 69018884 D DE 69018884 T EP 0405660 A JP 2776960 B JP 3034539 A	09-01-1991 01-06-1995 07-12-1995 02-01-1991 16-07-1998 14-02-1991
US 5269879 A	14-12-1993	US 5658425 A	19-08-1997
EP 127188 A	05-12-1984	JP 1895081 C JP 6022212 B JP 59220925 A US 4529475 A	26-12-1994 23-03-1994 12-12-1984 16-07-1985



## ANISOTROPIC ETCHING OF ORGANIC-CONTAINING INSULATING LAYERS

## FIELD OF THE INVENTION

- 5 The present invention is related to the process of semiconductor device fabrication. More in particular, methods including tools and chemistries for anisotropic dry etching of low k polymers are disclosed. These etching processes can be used for definition of via holes and trenches in different interconnect architectures.

## 10 BACKGROUND OF THE INVENTION

- The ongoing focus on miniaturisation and the increasing complexity and speed requirements of integrated circuits demand for a continuous higher density integration. To achieve this, there is an ongoing downscaling of the dimensions of the active devices as well as of the structures interconnecting these devices. These interconnect structures can comprise multiple metal levels which are, dependent on the aimed interconnect pattern, either separated one from another by means of interlevel insulating layers or connected one to the other by means of a conductive connection through the insulating layer. Intra-level insulating layers are used to provide isolation within a metal level. Besides this downscaling of the dimensions, additional measures are required to be able to meet the stringent speed specifications like e.g. the signal delay. Conventionally the metal levels are Aluminum layers while the insulating layers are oxide layers. In order to reduce the signal delay one can choose a metal layer with a higher conductivity compared to Aluminum, e.g. a Cu-containing metal layer, and/or choose insulating layers with a lower dielectric constant compared to oxide layers.

- This demand for insulating layers with a low dielectric constant has lead to an intensified search for new low K materials to be used as insulating layers. A low  $\epsilon$  material, a low K material and a material with a low permittivity are all alternative expressions for a material with a low dielectric constant, at least for the purposes of this disclosure. The most desirable material should have a low K value, low mechanical stress, high thermal stability and low moisture absorption. Furthermore, the desired material should be selected based on the compatibility with state-of-the-art semiconductor processing steps and tools. Among these new materials are the organic spin-on materials, having a K value in the range from 2.5 to 3, the porous polymers, and the inorganic low-K materials as e.g. xerogels having a K value typically lower than 1.5. The organic materials are of

particular interest because they feature simplified processing, excellent gap-fill and planarization.

Nowadays, there are two major ways of fabricating interconnect structures. In the conventional way as a start a conductive layer, e.g. a metal layer, is formed on an insulating layer (or on the substrate) and patterned thereafter usually by means of reactive ion etching (RIE). Another way is the damascene technology. In the damascene technology, first an insulating layer is deposited and patterned and thereafter a metal layer is deposited to fill the openings, eventually followed by a planarization step to remove the metal excess. The damascene technology has the additional advantage that the difficult metal RIE step is avoided. Damascene processing reduces the problem to dry etching of an insulating layer or a stack of insulating layers. This technique allows to build up horizontal metal patterns as well as vertical metal connections in the surrounding insulating layers. These vertical metal connections are required in order to be able to provide a conductive connection between two horizontal metal patterns being processed in different metal levels. To provide such a connection, usually first openings have to be formed in the insulating layer or in the stack of insulating layers between two different metal levels and filled thereafter with a conductive material. Examples of such openings are via holes or contact holes or trenches. To meet the high density integration requirements, the diameter of these openings is continuously decreasing, while at the same time the aspect ratio of these openings is increasing. Due to the small diameter and the high aspect ratios, the creation of these openings, especially the lithographic steps and the etchings steps involved, is a critical process. Therefore, etching of polymers used as insulating layers requires highly anisotropic etching capabilities.

US patent 5,269,879 is related to the etching of silicon oxide, silicon nitride or oxynitride layers in order to create a via hole extending through such a layer to an underlying electrically conductive layer. Particularly plasma etching is disclosed in an ambient including a fluorine-containing gas, a small amount of a passivating gas, i.e. nitrogen, and eventually an inert gas. This passivating gas is added to the plasma to prevent the sputtering of the underlying electrically conductive layer.

US patent 5,176,790 is related to the etching of mainly silicon oxide, silicon nitride or oxynitride layers in order to create a via hole extending through such a layer to an underlying electrically conductive layer. Particularly plasma etching is disclosed in an ambient including a fluorine-containing gas, a nitrogen-containing gas, and eventually an inert gas. This nitrogen-containing gas is added to the plasma to prevent the sputtering of



the underlying electrically conductive layer. However the amount of nitrogen-containing gas in the ambient is limited. This amount ranges from 1 volume part of nitrogen-containing gas per 2 volume parts of fluorine-containing gas to 1 volume part of nitrogen-containing gas per 15 volume parts of fluorine-containing gas.

## SUMMARY OF THE INVENTION

Etching of insulating layers in semiconductor processing requires highly anisotropic etching capabilities in order to be able to create sub 0.5  $\mu\text{m}$  openings such as via holes, trenches and contact holes. A method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. Preferably, this organic-containing insulating layer comprises at least one unsaturated carbon bond. Examples of organic-containing insulating layer comprising at least one unsaturated carbon bond are organic-containing insulating layers comprising at least one phenyl group. Typical examples are the benzocyclobutarenes, poly arylene ether, aromatic hydrocarbon, and polyimides. These openings are created substantially without depositing etch residues on the exposed layers by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a fluorine-containing gas and an inert gas. Substantially without etch residues means that a limited amount of etch residues can be formed on the exposed layers but that their composition is such that they can easily be removed selective to the organic-containing insulating layer after the openings have been created in subsequent etch or cleaning steps and that they do not affect the anisotropy of the plasma etching. While the plasma etching proceeds, the process conditions are such that the side walls of the openings are fluorinated which advantageously affects the anisotropy of said plasma etching. To obtain anisotropic plasma etching, preferably the spontaneous etching is negligible, while the etch reaction is effectively stimulated by ion bombardment. In other words, the lateral etch rate should be negligible small compared to the vertical etch rate. Particularly by exposing the side walls of the openings to the fluorine-containing gaseous mixture, the chemical composition of the organic-containing insulating layer at the side walls of the openings is modified. This modification results in an increase of the chemical resistance of the fluorinated part of the organic-containing insulating layer, i.e. at the side walls of the openings thereby enhancing the anisotropy of the plasma etching. Plasma etching includes plasma-assisted dry etching as well as reactive ion etching (RIE). The plasma etching of the organic-containing insulating layer can be performed using a patterned bilayer as an etch mask, said bilayer comprising a resist hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said resist hard mask layer. Particularly, said resist hard mask layer is a silicon oxide, or a silicon nitride, or a silicon oxynitride layer, or a silicon carbide layer, or a silicon oxycarbide layer. For the purpose of this disclosure a resist hard mask layer is a layer being used as an etch mask layer or an etch stop layer to selectively remove a resist layer. The plasma etching is preferably but not necessarily selective to said resist hard mask layer. The process conditions are such that a highly anisotropic plasma etch is performed

featuring substantially no undercut of the hard mask layer and substantially with the conservation of the original hard mask profile.

5 In an embodiment of the invention, the openings created in the organic-containing insulating layers comprise at least one via hole, said via hole extending through said insulating layer to an underlying conductive layer or a barrier layer. The plasma etching method of the present invention is selective to this underlying layer. In other words excess removal of this underlying layer is prevented. This underlying conductive and/or barrier layer can be a layer of Ti, TiN, Ta, TaN, Co, silicon nitride, silicon carbide, silicon  
10 oxycarbide, Pt, W, Al, Cu or an alloy of Al or Cu, or any other low resistivity material.

In another embodiment of the invention, the plasma etching method removes the resist layer during the creation of the openings in the organic-containing insulating layers. However in this case, the resist hard mask layer has to be a hard mask layer. For the  
15 purpose of this disclosure, a hard mask layer is defined as a layer which can be etched selective to the underlying layer, i.e. the organic-containing insulating layer. By doing so, a resist strip after the openings have been created is avoided. Therefore the thickness of the resist layer has to be chosen in accordance with the precise etch conditions and the thickness of the insulating layer. Particularly, this is important when the organic containing  
20 insulating layers are silicon-free layers because these silicon-free layers are very sensitive for subsequent etch steps or cleaning steps.

Yet in another embodiment of the invention, the plasma etching method only partly removes the resist layer during the creation of the openings in the organic-containing  
25 insulating layers. The thickness of the resist layer is chosen in accordance with the precise etch conditions and the thickness of the organic-containing insulating layer and such that there is still some resist left-over when the openings are created. Afterwards the resist left-over is removed e.g. using a solvent stripper, or an oxygen-containing plasma, or a combination thereof. Particularly this oxygen-containing plasma can be an oxygen plasma.  
30 This resist removal can be done substantially without consequences for the side walls of the organic-containing insulating layer at the openings provided that said polymer layer is not too sensitive for said oxygen-containing plasma. A typical example of such a layer which is not too sensitive for an oxygen-containing plasma is a layer selected from the group of the benzocyclobutarenes.

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In a further embodiment of the invention, the gaseous mixture in the reaction chamber further comprises an oxygen-containing gas. Examples of such an oxygen-

containing gas are O<sub>2</sub>, CO, CO<sub>2</sub> and SO<sub>2</sub>, but the invention is not limited hereto. By the addition of a small amount of oxygen to the gaseous mixture, the etch rate is increased.

5 In still a further embodiment of the invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created substantially without depositing etch residues by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a fluorine-containing gas. So no inert gas is present in said gaseous mixture.

10 In a second aspect of the present invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a oxygen-containing gas and an inert gas. The ratio between said oxygen-containing gas and said inert gas in said  
15 gaseous mixture is chosen such that the spontaneous etch rate is substantially zero. So the use of fluorine is avoided which can be beneficial for the further processing because amongst others, fluorine is known to stimulate corrosion, e.g. especially for Cu this can be an issue.

20 The plasma etching of the organic-containing insulating layer, according to the present invention, can be performed using a patterned bilayer as an etch mask, said bilayer comprising a hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said hard mask layer. The plasma etching method has a high selectivity to the hard mask layer formed on the polymer layer. The plasma etch  
25 process creates openings in the organic-containing insulating layer and simultaneously selectively removes the resist layer thereby avoiding a resist strip after etching. Preferably, this organic-containing insulating layer is an organic polymer layer with a low K value. Particularly, this organic-containing insulating layer can be a silicon-free polymer layer.

30 In an embodiment of the invention the oxygen-containing gas in the gaseous mixture is O<sub>2</sub> and the inert gas in the gaseous mixture is nitrogen. The ratio of the amount of nitrogen in said gaseous mixture to the amount of oxygen in said gaseous mixture is preferably in the range from about 10:1 to about 2:1, or from about 30:1 to about 1:1, or from about 50:1 to about 1:1.

35 In another embodiment of the invention a two-step anisotropic etch process is disclosed, wherein in a first step a first part of an opening is created by means of

anisotropic plasma etching using a gaseous mixture comprising a fluorine-containing gas and an inert gas, while in a second step the second part of said opening is etched by means of anisotropic plasma etching using a gaseous mixture comprising an oxygen-containing gas and an inert gas to thereby complete said opening and simultaneously selectively remove the resist.

In a third aspect of the present invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising HBr and an additive, said additive passivating the exposed parts of the insulating layer, i.e. the side walls. Typical examples of such an additive are an inert gas, like N<sub>2</sub>, Ar, He, Xe, Krypton or an oxygen-containing gas, like O<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>O, NO<sub>2</sub>, SO<sub>2</sub>, but the invention is not limited hereto. Preferably, this organic-containing insulating layer is an organic polymer layer with a low K value.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 represents afterglow etch rates of planar SiLK (2) and BCB (1) layers for different NF<sub>3</sub>/O<sub>2</sub> flow ratios.

Figure 2 represents, according to an embodiment of the invention, the etch rate of BCB (Cyclotene 5021<sup>TM</sup>) in a plasma ambient comprising a mixture of NF<sub>3</sub>, O<sub>2</sub> and He versus the percentage of NF<sub>3</sub>. The total gas flow was 115 sccm, whereas the pressure in the chamber was 1.30 Torr. The He flow was kept constant and equal to 65 sccm. The flows of NF<sub>3</sub> and O<sub>2</sub> were chosen complementary and were varied between 0 and 50 sccm, whereby the sum of the NF<sub>3</sub> flow and the O<sub>2</sub> flow was kept constant and equal to 50 sccm. The percentage of NF<sub>3</sub> in the figure is the relative amount of NF<sub>3</sub> compared to the amount of NF<sub>3</sub> and O<sub>2</sub> without taking into account He.

Figure 3 represents the change in refractive index of SiLK and BCB as a function of etch time in a NF<sub>3</sub> afterglow plasma.

Figure 4 represents etch rates of SiLK and BCB in RIE conditions with changing SF<sub>6</sub>/O<sub>2</sub> gas flow ratios (0 = pure O<sub>2</sub> diluted in N<sub>2</sub>, 100 = pure SF<sub>6</sub> diluted in N<sub>2</sub>).

Figure 5 represents a SEM picture of the via holes in an organic-containing insulating layer (7), i.e. a BCB layer, after plasma etching according to an embodiment of the invention in an ambient comprising  $\text{SF}_6$  and  $\text{N}_2$ . The picture shows a  $\text{SiO}_2$  layer (8), remaining resist (9), intact Ti/TiN barrier layer (6) on a conductive AlSiCu layer (5). Layer (4) is again a Ti/TiN barrier layer. No undercut of the  $\text{SiO}_2$  layer can be detected.

Figure 6 represents a SEM picture of via holes in an organic-containing insulating layer (7), i.e. a SILK layer, after plasma etching according to an embodiment of the invention in an ambient comprising  $\text{O}_2$  and  $\text{N}_2$ , showing intact  $\text{SiO}_2$  layer (8), intact Ti/TiN barrier layer (6) on a conductive AlSiCu layer (5). No undercut of the  $\text{SiO}_2$  layer can be detected.

Figure 7 represents a SEM picture of trenches in an organic-containing insulating layer (7), i.e. a SILK layer, after plasma etching according to an embodiment of the invention in an ambient comprising  $\text{N}_2$  and  $\text{O}_2$  at a ratio of 5:1, showing intact  $\text{SiO}_2$  layer (8). No undercut of the  $\text{SiO}_2$  layer can be detected.

Figure 8 represents, according to an embodiment of the invention, a detailed description of the processing steps involved to create a particular interconnect structure, i.e. a dual-damascene structure.

Figure 9 represents a SEM picture of trenches in an organic-containing insulating layer (7), i.e. a SILK layer, after a two-step plasma etching according to an embodiment of the invention, showing intact  $\text{SiO}_2$  layer (8). No undercut of the  $\text{SiO}_2$  layer can be detected.

## DETAILED DESCRIPTION OF THE INVENTION

In relation to the appended drawings the present invention is described in detail in the sequel. It is apparent however that a person skilled in the art can imagine several other equivalent embodiments or other ways of executing the present invention, the spirit and scope of the present invention being limited only by the terms of the appended claims.

In a first aspect of the present invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created substantially without depositing etch residues by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a fluorine-containing gas and an inert gas. Preferably, this organic-containing insulating layer comprises at least one unsaturated carbon bond. Examples of organic-containing insulating layer comprising at least one unsaturated carbon bond are organic-containing insulating layers comprising at least one phenyl group. Typical examples are the benzocyclobutenes, e.g. Cyclotene 5021<sup>TM</sup> from Dow Chemical with chemical formulation divinyl siloxane benzocyclobutane (BCB), poly arylene ether, e.g. FLARE<sup>TM</sup> II, aromatic hydrocarbon, e.g. SILK<sup>TM</sup>. The substrate can be a partly processed or a pristine wafer or slice of a semi-conductive material, like Si or Ga As or Ge, or an insulating material, e.g. a glass slice, or a conductive material. Said substrate can comprise a patterned conductive layer. Particularly, in case said substrate is a partly processed wafer or slice; at least a part of the active and/or passive devices can already be formed and/or at least a part of the structures interconnecting these devices can be formed.

To obtain anisotropic plasma etching, preferably the spontaneous etching is limited or negligible, while the etch reaction is effectively stimulated by ion bombardment. In other words, the lateral etch rate should be negligible small compared to the vertical etch rate. Particularly by exposing the side walls of the openings, i.e. the surface of the organic-containing insulating layer comprising at least one phenyl group at these side walls of these openings, to the fluorine-containing gaseous mixture during the plasma etching, these side walls are fluorinated which advantageously affects the anisotropy of said plasma etching. By doing so, the chemical composition of the organic-containing insulating layer comprising at least one unsaturated carbon bond is modified at the side walls of the openings. Particularly, organic-containing insulating layers comprising phenyl groups contain such unsaturated carbon bonds. These carbon bonds, which can be attacked by reactive species such as atomic fluorine generated in a plasma or another ambient comprising active fluorine. Said active fluorine can abstract hydrogen from carbon in said

phenyl groups. Therefore, the method involves a formal replacement of hydrogen by fluorine. Furthermore, due to the small size of the fluorine atoms, they can easily diffuse through the insulating layer. Consequently the replacement of hydrogen by fluorine is not limited to the surface of the layer but can extend also further in the layer. Fluorine is the most electronegative and the least polarizable element on the periodic table. The incorporation of fluorine in the insulating layer at the side walls of the openings makes the fluorinated part of the insulating layer less polarizable leading to an increase in chemical resistance and a decrease of the K value of said part, said part starts at a surface and extends in the insulating layer with elapsing exposure time. So particularly, this in-situ fluorination results in an increase of the chemical resistance of the fluorinated part of the organic-containing insulating layer, i.e. at the side walls of the openings thereby enhancing the anisotropy of the plasma etching. It should be clear however that during the plasma etching the bottom side of the openings, i.e. a surface of the insulating layer at the etch front of the opening is also exposed to the gaseous mixture comprising fluorine. But contrary to the side walls, at the bottom side of the openings fluorination is prevented or at least the effect of the fluorination is nullified by the ion bombardment. Plasma etching includes plasma-assisted dry etching as well as reactive ion etching (RIE). The plasma etching of the organic-containing insulating layer can be performed using a patterned bilayer as an etch mask, said bilayer comprising a resist hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said hard mask layer. Particularly, said resist hard mask layer can be a silicon oxide, or a silicon nitride, or a silicon oxynitride, or a silicon carbide, or a silicon oxycarbide. By doing so a highly anisotropic plasma etch is performed featuring substantially no undercut of the resist hard mask layer and with the conservation of the original resist hard mask profile.

The pressure in the reaction chamber is typically between 1 mTorr and 100 mTorr, or between 1mTorr and 300 mTorr, or between 1 mTorr and 5 Torr. The setting temperature is typically between -10 °C and 50 °C, -30 °C and 50 °C, or -60 °C and 70 °C. This setting temperature is the temperature as set on the heating/cooling source. The actual temperature in the reaction chamber can be higher dependent on the plasma conditions. Typical examples of fluorine-containing gases are SF<sub>6</sub>, or NF<sub>3</sub>, or C<sub>2</sub>F<sub>6</sub>, or CF<sub>4</sub> or CHF<sub>3</sub> or CH<sub>3</sub>F or CH<sub>2</sub>F<sub>2</sub> or mixtures thereof. The inert gas can be helium or argon or krypton or nitrogen or xenon or krypton. The inert gas is preferably nitrogen. More preferably, the ratio of the amount of nitrogen in said gaseous mixture to the amount of fluorine-containing gas in said gaseous mixture is larger than 2:1.



In case the opening is a via hole, the plasma etching is performed until the surface of an underlying conductive layer or an underlying barrier layer is reached while preventing excess removal of the underlying layer. This underlying conductive and/or barrier layer can be a layer of Ti, TiN, Ta, TaN, Co, silicon nitride, silicon carbide, silicon oxycarbide, Pt, W, Al, Cu or an alloy of Al or Cu, or any other low resistivity material.

As an example, an anisotropic plasma etch process to create openings in a BCB layer is disclosed.

Experimental conditions are:

etch tool : high density plasma reactor (TCP 9400)

gaseous mixture for the plasma etch : SF<sub>6</sub> and N<sub>2</sub>

etch conditions in chamber: 15 mTorr

TCP power : 700 watt

bottom power : 100 watt

hard mask layer is a PECVD oxide layer with a thickness of 250 nm

thickness of the resist layer (Sumitomo I-line resist): 1.2  $\mu$ m

thickness of BCB layer: 0.7  $\mu$ m

underlying layer: TiN layer

set-point temperature : 20 °C

Under these conditions the BCB layer was etched with an etch rate of 500 nm/min, yielding a highly anisotropic etch profile and substantially no hard mask undercut (figure 5). Furthermore the resist hard mask profile was kept intact and there was substantially no TiN loss. When reaching the surface of the TiN layer the thickness of the remaining resist left-overs was about 0.1  $\mu$ m. These resist left-overs can be removed by a subsequent etching step without attacking the other materials present on the wafer, particularly the BCB. Then, eventually, a cleaning step can be performed using diluted H<sub>2</sub>SO<sub>4</sub> to remove the residues without attacking the other materials present on the wafer. Alternatively, instead of H<sub>2</sub>SO<sub>4</sub> EKC 265 or a combination of H<sub>2</sub>SO<sub>4</sub> and EKC 265 can be used.

With this etch chemistry, resist hard mask undercut is prevented due to the fluorination of at least a part of the BCB layer. This fluorination is obtained by exposure of the side walls of the BCB layer to an ambient comprising fluorine. Said fluorination increases the chemical and mechanical resistance of said BCB as clearly supported by figures 1, 2 and 3.

Figure 1 shows the etch rate of a planar BCB layer (1) and a SILK layer (2) under afterglow conditions, i.e. without ion bombardment, in a gaseous mixture comprising a fluorine-containing gas, being  $\text{NF}_3$ , and an oxygen-containing gas, being  $\text{O}_2$ . It is observed that the etch rate in pure fluorine-containing plasma is substantially zero. It is also observed that this exposure affects only a part of the layer, said part starting at the exposed surface of the layer and extending into the layer. The thickness of said fluorinated part of the film depends on the atomic fluorine concentration, the fluorination time, i.e. the exposure time, and the temperature. This observation confirms the expectations because the fluorination is a diffusion limited process. The fluorination of said part of the BCB layer, leads to a change of refractive index and chemical composition of said fluorinated part of the BCB layer. This is also observed for SILK films and Flare-II films. As depicted in Fig. 2, the etch rate for etching a fluorinated BCB film (3) in a  $\text{O}_2/\text{NF}_3$  afterglow plasma can be substantially lower than the etch rate for etching pristine BCB films (1), dependent on the  $\text{O}_2/\text{NF}_3$  ratio. The change of the refractive index (figure 3) is also indicative for the fluorination of the BCB layer under pure  $\text{NF}_3$  afterglow conditions. Lowering of the refractive index results in a lowering of the K-value. From these observations in an afterglow plasma, one can conclude that lateral etching in a plasma etch process, e.g. RIE, can be controlled by the choice of the right process chemistry. The vertical etch rate however will be higher in RIE as compared to afterglow because energy is still provided to the surface by means of ion bombardment. The vertical etch rates obtained in RIE for  $\text{SF}_6/\text{N}_2$  chemistries are shown in figure 4. From the figures, one can conclude that working under oxygen free etch conditions allows sufficient etch rate (vertical) with substantially zero etch rate in the lateral direction.

In a second aspect of the present invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a oxygen-containing gas and an inert gas. Preferably, this organic-containing insulating layer is a low K polymer layer. Particularly, this organic-containing insulating layer can be a silicon-free polymer layer. Typical examples are poly arylene ether, i.e. FLARE<sup>TM</sup> II, aromatic hydrocarbon, i.e. SILK<sup>TM</sup>. To obtain anisotropic plasma etching, preferably the spontaneous etching is limited or negligible, while the etch reaction is effectively stimulated by ion bombardment. In other words, the lateral etch rate should be negligible small compared to the vertical etch rate. As can be deduced from fig. 1 the spontaneous etch rate of a planar SILK layer (2) and a planar BCB layer (1) under afterglow conditions, i.e. without ion bombardment, in a pure oxygen ambient is, although, below 100 nm per minute, far too high making such a

pure oxygen ambient unsuited for anisotropic plasma etching. However, by introducing an appropriate amount of an inert gas the spontaneous etching rate can be reduced to substantially zero. The plasma etching of the organic-containing insulating layer, according to the present invention, can be performed using a patterned bilayer as an etch mask, said bilayer comprising a hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said hard mask layer. The plasma etching method has a high selectivity to the hard mask layer formed on the polymer layer. Particularly, said hard mask layer can be a silicon oxide, or a silicon nitride, or a silicon oxynitride, or a silicon carbon, or a silicon oxycarbon layer. The plasma etch process creates openings in the organic-containing insulating layer and simultaneously removes the resist layer thereby avoiding a resist strip after etching. By doing so a highly anisotropic plasma etch is performed featuring substantially no undercut of the hard mask layer, selective to the hard mask layer and with the conservation of the original hard mask profile. Preferably (fig. 7), the side walls of the openings are slightly positively sloped yielding a better performance and reliability in the subsequent processing steps, as e.g. filling the opening with a metal.

The pressure in the reaction chamber is typically between 1 mTorr and 100 mTorr, or between 1mTorr and 300 mTorr, or between 1 mTorr and 5 Torr. The setting temperature is typically between -10 °C and 50 °C, -30 °C and 50 °C, or -60 °C and 70 °C. This setting temperature is the temperature as set on the heating/cooling source. The actual temperature in the reaction chamber can be higher dependent on the plasma conditions. Preferably the oxygen-containing gas is O<sub>2</sub> but the invention is not limited hereto. The inert gas can be helium or argon or krypton or xenon or nitrogen. The inert gas is preferably nitrogen. More preferably, the ratio of the amount of nitrogen in said gaseous mixture to the amount of oxygen in said gaseous mixture is in the range from 10:1 to 2:1 or from 30:1 to 1:1.

In case the opening is a via hole, the plasma etching is performed until the surface of the underlying conductive layer or the underlying barrier layer is reached while preventing excess removal of the underlying layer. This underlying conductive and/or barrier layer can be a layer of Ti, TiN, Ta, TaN, Co, silicon nitride, silicon carbide, silicon oxycarbide, Pt, W, Al, Cu or an alloy of Al or Cu, or any other low resistivity material.

In an embodiment of the invention, as an experimental example, an anisotropic etch process on a silicon-free polymer layer, i.e. a SILK layer is disclosed. Experimental conditions are:

etch tool : high density plasma reactor (TCP 9100)  
gaseous mixture for the plasma etch : O<sub>2</sub> and N<sub>2</sub>  
etch conditions in chamber: 5 mTorr  
TCP power : 400 watt  
5 bottom power : 200 watt  
hard mask layer is a PECVD oxide layer with a thickness of 250 nm  
thickness of the resist layer (Sumitomo I-line): 1.2  $\mu$ m  
thickness of SILK layer: 1.1  $\mu$ m  
underlying layer: TiN layer  
10 set-point temperature : 20 °C

Under these conditions the SILK layer was etched with an etch rate of 500 nm/min, yielding via holes (fig. 6) with a highly anisotropic etch profile and substantially no hard mask undercut. Furthermore the hard mask profile was kept intact and there was  
15 substantially no TiN loss. When reaching the surface of the TiN layer the resist layer was totally removed. Then a cleaning step was performed using diluted H<sub>2</sub>SO<sub>4</sub> to remove the residues without attacking the other materials present on the wafer. Alternatively, instead of H<sub>2</sub>SO<sub>4</sub>, EKC 265 or a combination of H<sub>2</sub>SO<sub>4</sub> and EKC 265 or an SPM solution can be used.

20 In another embodiment of the invention, prior to the step of anisotropic plasma etching of an organic-containing insulating layer in an ambient comprising an oxygen-containing gas and an inert gas, a first part of an opening is created in said organic-containing insulating layer by plasma etching in an ambient comprising a fluorine-containing gas and an inert gas. In fact a two-step anisotropic etch process is disclosed (as  
25 in fig.9) wherein in a first step a first part of an opening is created by means of anisotropic plasma etching using a gaseous mixture comprising a fluorine-containing gas and an inert gas, while in a second step the second part of said opening is etched by means of anisotropic plasma etching using a gaseous mixture comprising an oxygen-containing gas  
30 and an inert gas to thereby complete said opening and simultaneously selectively remove the resist. The openings formed by this two-step etch process have slightly positively sloped side walls. As an example (figure 8), a particular dual-damascene structure is described. During the fabrication of such a structure the method of the present invention is utilised. It should be clear however that the invention is not limited to this particular structure but the  
35 present invention can be applied for any isolation or interconnect structure comprising organic-containing insulating layers wherein openings have to be created. According to the example (fig.8):

A first dielectric layer (12), i.e. an organic polymer layer comprising phenyl groups is formed on a substrate (11) comprising a patterned conductive layer (10). Said conductive layer can be a single conductive layer or a combination of a conductive layer and a barrier layer. Examples of such polymers are the benzocyclobutarenes, i.e. benzocyclobutene (BCB) commercially available as Cyclotene 5021<sup>TM</sup>, poly arylene ether, i.e. FLARE<sup>TM</sup> II, aromatic hydrocarbon, i.e. SILK<sup>TM</sup>, polyimides.

A first hard mask layer (13), e.g. a silicon oxide or a silicon nitride or a silicon oxynitride layer or a SiC layer, is formed on this organic polymer film. Then a patterned resist layer (14) is formed thereon (fig.8, step a)). Further, said first hard mask layer is patterned (fig.6, step b)) using said patterned resist layer as a mask and said second resist layer is removed.

A second dielectric layer, i.e. an organic-containing insulating layer comprising at least one phenyl group (15), is formed (step c)) on the patterned first hard mask layer. A patterned bilayer (16) is formed (step d)) on said second dielectric layer. This bilayer comprises a second hard mask layer, being formed on said second dielectric layer, and a second resist layer being formed on said second hard mask layer.

The first and the second dielectric layer can be etched by means of the anisotropic plasma etching method of the present invention. There are at least two possibilities.

As a first possibility, a first part of the openings can be formed by plasma etching said second dielectric layer in a gaseous mixture comprising a fluorine containing gas and an inert gas using the patterned bilayer as an etch mask which can result in the formation of a first part of a trench and a first part of a via hole. In such case, the first hard mask layer not necessarily functions as an etch stop layer. The thickness of the second resist layer is chosen in accordance with the etch time such that when this first timed etch is stopped there is still some resist left and said first hard mask layer is not yet reached. Thereafter the etch in said second dielectric layer is continued by plasma etching in a gaseous mixture comprising an oxygen-containing gas and an inert gas. This second etch is selective to said first and said second hard mask layer thereby preventing the extension from the trench in the first dielectric layer (step e)). The first dielectric layer is then etched in a gaseous mixture comprising an oxygen-containing gas and an inert gas using the patterned first hard mask layer as a mask to form a via hole i.e. exposing the surface of the underlying conductive layer (step e)).

As a second possibility, the openings can be formed by plasma etching said second dielectric layer in a gaseous mixture comprising an oxygen-containing gas and an inert gas using the patterned bilayer as an etch mask. This etch is selective to said first and said second hard mask layer thereby preventing the extension from the trench in the first dielectric layer (step e)). The first dielectric layer is then etched in a gaseous mixture

comprising an oxygen-containing gas and an inert gas using the patterned first hard mask layer as a mask to form a via hole i.e. exposing the surface of the underlying conductive layer (step e)). The etching of the first and second dielectric layer can be performed using a single etch step or two subsequent etch steps.

5 Both possibilities have the common advantage that the second resist layer is completely and selectively removed.

Thereafter said second hard mask layer can be removed (as in fig. 8 step e)) or not.

10 A conductive layer, e.g. an alloy of or pure Al, Cu, Ag, Pt, Co, Ti, Ni or Au, or a combination of a conductive layer (18) and a barrier layer (17), like e.g. a Ti-containing layer or a Co-containing or a Ni-containing layer or a Ta-containing layer, can be deposited (steps f) and g)) thereby filling the via hole in the first and second dielectric layer and the trench in the second dielectric layer.

15 In a third aspect of the present invention, a method is disclosed for forming at least one opening in an organic-containing insulating layer formed on a substrate. These openings are created by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising HBr and an additive, said additive passivating the exposed parts of the insulating layer, i.e. the side walls. Typical examples of such an additive are an inert gas, like N<sub>2</sub>, Ar, He, Xe, krypton or an oxygen  
20 containing gas, like O<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>O, NO<sub>2</sub>, SO<sub>2</sub>, but the invention is not limited hereto. In fact, a wide variety of additives can be used for increasing the etch rate and/or for additional side wall passivation possibly resulting in positively sloped profiles. In an embodiment of the invention, said gaseous mixture can further comprise fluorine-containing gases in order to increase the etch rate while keeping the selectivities and profiles  
25 substantially unchanged by balancing the gas flows.

In another embodiment of the invention, said gaseous mixture can further comprise chlorine-containing gases in order to increase the etch rate while keeping the profiles substantially unchanged and allowing a slight decrease of the selectivities by balancing the  
30 gas flows.

The organic-containing insulating layer can be plasma etched using the combination of a patterned hard mask layer and a patterned resist layer as an etch mask by means of plasma etching. The organic-containing insulating layer can be a polymer layer, preferably  
35 having a low permittivity. Particularly also silicon-containing polymer layers can be used. The pressure in the chamber is typically between 1 mTorr and 50 mTorr or between 1 mTorr and 5 Torr.. By doing so a highly anisotropic etch is performed featuring

substantially no undercut of the hard mask layer, selective to the hard mask layer and with the conservation of the original hard mask profile. Furthermore, in case said opening is a via hole, this highly anisotropic etch is selective to the underlying conductive layer or barrier layer.

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Particularly, towards the silicon-containing polymers, HBr will help in obtaining higher etch rates by generating SiBr etch products which can be volatilized by means of ion bombardment. At the same time, lateral etching will be substantially inhibited by the formation of  $\text{SixBr}_y\text{O}_z$  passivation layers, x, y and z being positive whole numbers.

10 Possibly also C can be incorporated in these passivation layers. These passivation layers are stable as long as there is no exposure to ion bombardment. Particularly, the side walls of the via holes and/or trenches are not exposed to such an ion bombardment. The plasma etch process will have a very high selectivity towards hard mask materials allowing the resist to be removed during the etch process with conservation of the hard mask thickness and  
15 profile. As a consequence, this process will allow much thinner hard masks to be used for the formation of via holes and/or trenches. Selectivity both to the hard mask layer and to the underlying conductive layer can be obtained by controlling the ion energy.

Towards the silicon-free polymers, this plasma etch process will allow improved profiles because of the limited lateral etch rate. This will allow high over-etch times  
20 whenever needed. The plasma etch process will have a very high selectivity towards hard mask materials allowing the resist layer to be removed during the etch process with conservation of the hard mask thickness and profile. As a consequence, this process will allow much thinner hard mask layers to be used for the formation of via holes and/or trenches. Selectivity both to hard mask layer and eventually to the underlying conductive  
25 layer can be obtained by controlling the ion energy.

## WHAT IS CLAIMED IS:

1. A method for forming at least one opening in an organic-containing insulating layer, comprising the steps of:
  - 5       creating said opening by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a fluorine-containing gas and an inert gas; and
  - controlling said plasma etching, while creating said opening, in a manner that substantially no etch residues are deposited and that the side walls of said opening are
  - 10       fluorinated during said plasma etching to thereby enhance the anisotropy of said plasma etching.
2. A method as recited in claim 1, wherein said organic-containing insulating layer
- 15       comprises at least one unsaturated carbon bond.
3. A method as recited in claim 2, wherein said organic-containing insulating layer is selected from a group comprising the benzocyclobutarenes, poly arylene ether, aromatic hydrocarbon, and polyimides.
- 20   4. A method as recited in claim 1, wherein said plasma etching is performed using a patterned bilayer as a mask, said bilayer comprising a resist hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said resist hard mask layer.
- 25   5. A method as recited in claim 4, wherein said resist hard mask layer is a silicon oxide, or a silicon nitride, or a silicon oxynitride, or a silicon carbide, or a silicon oxycarbide layer.
6. A method as recited in claim 1, wherein said inert gas is nitrogen and wherein the ratio of the amount of nitrogen in said gaseous mixture to the amount of fluorine containing gas
- 30       in said gaseous mixture is larger than 2:1.
7. A method as recited in claim 1, wherein said fluorine-containing gas is  $\text{SF}_6$ , or  $\text{NF}_3$ , or  $\text{C}_2\text{F}_6$ , or  $\text{CF}_4$  or  $\text{CHF}_3$  or  $\text{CH}_3\text{F}$  or  $\text{CH}_2\text{F}_2$  or mixtures thereof.
- 35   8. A method as recited in claim 1, wherein said opening is at least one via hole, said via hole extending through said insulating layer to an underlying conductive layer or an underlying barrier layer.



9. A method as recited in claim 1, wherein said gaseous mixture further comprises an oxygen containing gas.

5 10. A method for forming at least one opening in an organic-containing insulating layer comprising the step of:

creating said opening by plasma etching said organic-containing insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising an oxygen-containing gas and an inert gas, said inert gas and said oxygen-containing gas being  
10 present in said gaseous mixture at a predetermined ratio, said ratio being chosen such that spontaneous etching is substantially avoided.

11. A method as recited in claim 10, wherein said organic-containing insulating layer is a low K organic polymer layer.

15 12. A method as recited in claim 10, wherein said plasma etching is performed using a patterned bilayer as a mask, said bilayer comprising a hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said resist hard mask layer.

20 13. A method as recited in claim 12, wherein said resist layer is selectively removed from said hard mask layer while creating said opening.

14. A method as recited in claim 10, wherein said oxygen-containing gas in said gaseous  
25 mixture is O<sub>2</sub> and said inert gas in said gaseous mixture is nitrogen.

15. A method as recited in claim 14, wherein said ratio of nitrogen in said gaseous mixture to oxygen in said gaseous mixture is in the range from 5:1 to 2:1.

30 16. A method as recited in claim 10, wherein prior to plasma etching in said reaction chamber containing said gaseous mixture, a first part of said opening is created by plasma etching said insulating layer in said reaction chamber containing a first gaseous mixture, said first gaseous mixture comprising a fluorine-containing gas and an inert gas;

controlling said plasma etching in said reaction chamber containing said first  
35 gaseous mixture, while creating said first part of said opening, in a manner that substantially no etch residues are deposited and that the side walls of said first part of said

opening are fluorinated during said plasma etching to thereby enhance the anisotropy of said plasma etching in said reaction chamber containing said first gaseous mixture.

17. A method as recited in claim 16, wherein said opening has positively sloped side walls.

## PATENT COOPERATION TREATY

PCT

## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

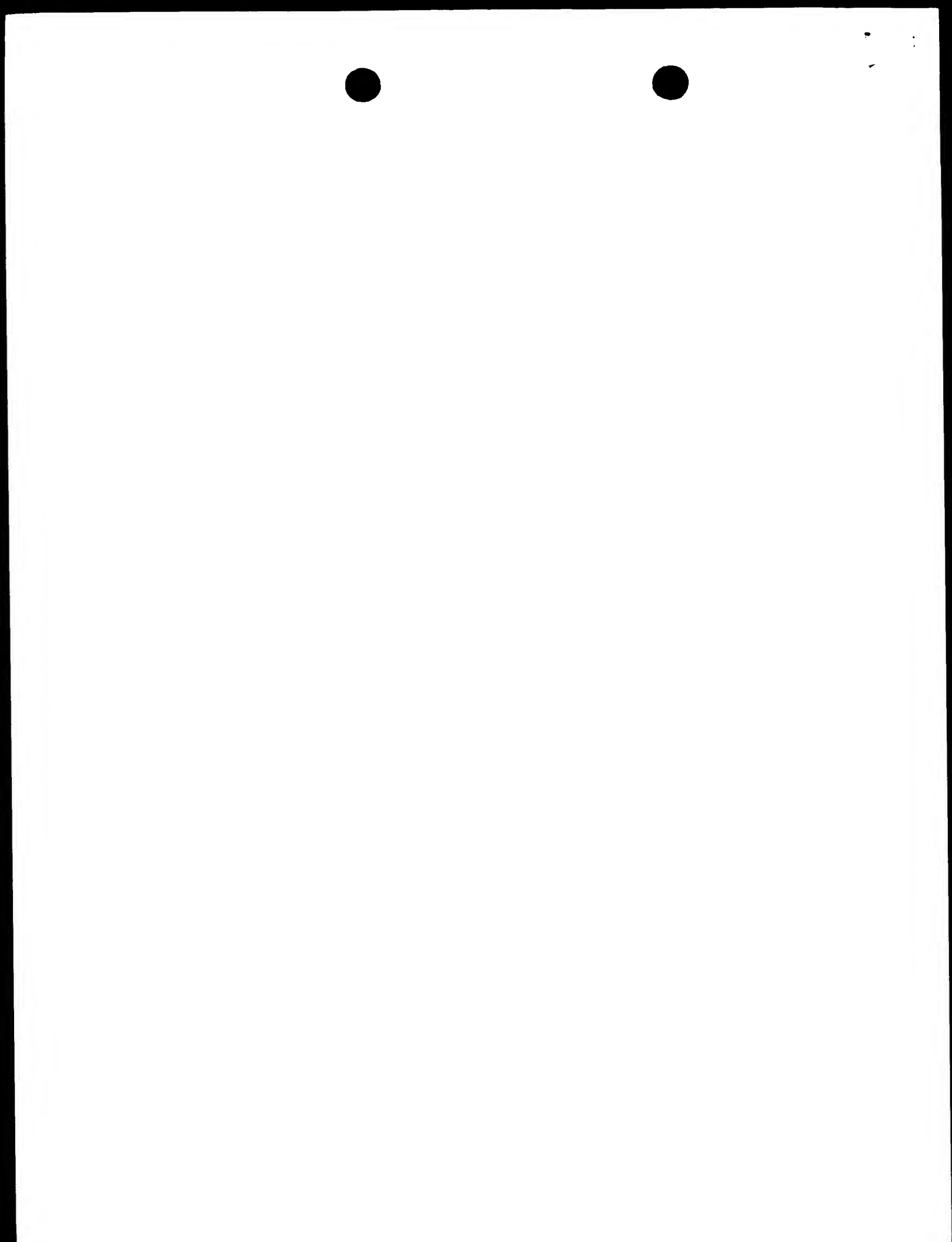
Applicant's or agent's file reference <b>P. IMEC. 85B/WO</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below	
International application No. <b>PCT/BE 98/00159</b>	International filing date (day, month, year) <b>22/10/1998</b>	(Earliest) Priority Date (day, month, year) <b>22/10/1997</b>
Applicant <b>INTERUNIVERSITAIR MICRO-ELEKTRONICA CENTRUM et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. ☐ **Certain claims were found unsearchable** (see Box I).
2. ☐ **Unity of invention is lacking** (see Box II).
3. ☐ The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international search was carried out on the basis of the sequence listing
  - ☐ filed with the international application.
  - ☐ furnished by the applicant separately from the international application.
    - ☐ but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
  - ☐ Transcribed by this Authority
4. With regard to the **title**, ☒ the text is approved as submitted by the applicant  
☐ the text has been established by this Authority to read as follows:
5. With regard to the **abstract**, ☒ the text is approved as submitted by the applicant  
☐ the text has been established, according to Rule 38 2(b), by this Authority as it appears in Box II. The applicant may, within one month from the date of mailing of this international Search Report, submit comments to this Authority.
6. The figure of the **drawings** to be published with the abstract is:
  - Figure No.          ☐ as suggested by the applicant.
  - ☐ because the applicant failed to suggest a figure.
  - ☐ because this figure better characterizes the invention.
  - ☒ None of the figures



A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 H01L21/3

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched classification system followed by classification symbols

IPC 6 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 816 196 A (LA COMBE) 11 June 1974 see Abstract see claims 1,2	1-15
X.P	PATENT ABSTRACTS OF JAPAN vol. 98, no. 5, 30 April 1998 & JP 10 012617 A (MITSUBISHI ELECTRIC CORP.), 16 January 1998 see Abstract	1-15
X	US 5 176 790 A (ARLEO ET AL.) 5 January 1993 cited in the application see claims 1,2,17,26; figures 1,2	1-9
	--- -/--	



Further documents are listed in the continuation of box C



Patent family members are listed in annex

## Special categories of cited documents

- A: document defining the general state of the art which is not considered to be of particular relevance
- E: earlier document but published on or after the international filing date
- L: document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- O: document referring to an oral disclosure, use, exhibition or other means
- P: document published prior to the international filing date but later than the priority date claimed

T: later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X": document of particular relevance, the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y": document of particular relevance, the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

&: document member of the same patent family

Date of the actual completion of the international search

12 February 1999

Date of mailing of the international search report

03/03/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5815 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31-651 epo nl  
Fax: (+31-70) 340-3016

Authorized officer

Thiele, N



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/BE 98/00159

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of documents with indication where appropriate of the relevant passages	Relevant to claim No
X	US 4 661 204 A (MATHUR ET AL.) 28 April 1987 see Abstract see claims 1.4-6 ----	1-15
X	US 5 173 442 A (CAREY) 22 December 1992 see column 4, line 3-8; claim 1; figures 1A-1F ---	1-15
X	US 5 358 902 A (VERHAAR ET AL.) 25 October 1994 see column 5, line 22-32 see claims 1.2.7 ---	1-15
A	DATABASE WPI Section Ch, Week 9530 Derwent Publications Ltd., London, GB: Class L03, AN 95-230257 XP002093190 & RU 2 024 991 A (MOLECULAR ELECTRON RES. INST.), 15 December 1994 see abstract ---	1-17
A	US 5 269 879 A (RHOADES ET AL. ) 14 December 1993 cited in the application see Abstract ---	1-17
A	EP 0 127 188 A (KK TOSHIBA) 5 December 1994 see claims 9-14 -----	1-17





## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/BE 98/00159

Patent document cited in search report		Publication date	Patent family members (s)	Publication date
US 3816196	A	11-06-1974	NONE	
US 5176790	A	05-01-1993	NONE	
US 4661204	A	28-04-1987	AU 581110 B AU 6549886 A EP 0244462 A JP 63501186 T WO 8702626 A	09-02-1989 19-05-1987 11-11-1987 28-04-1988 07-05-1987
US 5173442	A	22-12-1992	US 5091339 A US 5219787 A	25-02-1992 15-06-1993
US 5358902	A	25-10-1994	GB 2233494 A DE 69018884 D DE 69018884 T EP 0405660 A JP 2776960 B JP 3034539 A	09-01-1991 01-06-1995 07-12-1995 02-01-1991 16-07-1998 14-02-1991
US 5269879	A	14-12-1993	US 5658425 A	19-08-1997
EP 127188	A	05-12-1984	JP 1895081 C JP 6022212 B JP 59220925 A US 4529475 A	26-12-1994 23-03-1994 12-12-1984 16-07-1985



# PATENT COOPERATION TREATY

PCT

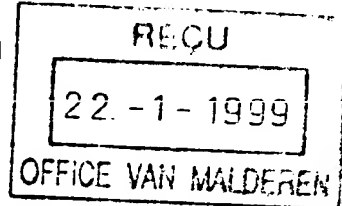
## NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

From the INTERNATIONAL BUREAU

To:

VAN MALDEREN, Joëlle  
Office Van Malderen  
Place Reine Fabiola 6/1  
B-1083 Brussels  
BELGIQUE



Date of mailing (day/month/year) 18 January 1999 (18.01.99)	<b>IMPORTANT NOTIFICATION</b>
Applicant's or agent's file reference P.IMEC.85B/WO	
International application No. PCT/BE98/00159	International filing date (day/month/year) 22 October 1998 (22.10.98)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 22 October 1997 (22.10.97)
Applicant INTERUNIVERSITAIR MICRO-ELEKTRONICA CENTRUM et al	

- The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
- An **asterisk(\*)** appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- The **letters "NR"** appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

<u>Priority date</u>	<u>Priority application No.</u>	<u>Country or regional Office or PCT receiving Office</u>	<u>Date of receipt of priority document</u>
22 Octo 1997 (22.10.97)	60/063,487	US	14 Janu 1999 (14.01.99)
12 Febr 1998 (12.02.98)	60/074,524	US	14 Janu 1999 (14.01.99)
18 May 1998 (18.05.98)	98870111.6	EP	NR

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

F. Gateau

Telephone No. (41-22) 338.83.38

002431648



# PATENT COOPERATION TREATY

From the INTERNATIONAL SEARCHING AUTHORITY

# PCT

To:  
OFFICE VAN MALDEREN  
Place Reine Fabiola 6/1  
1083 Bruxelles  
BELGIUM

NOTIFICATION OF TRANSMITTAL OF <b>REQU</b> THE INTERNATIONAL SEARCH REPORT OR THE DECLARATION  (PCT Rule 44.1)
- 8. - 3 - 1999 OFFICE VAN MALDEREN

Date of mailing <i>(day, month, year)</i> <div style="text-align: right; font-weight: bold;">03/03/1999</div>	
Applicant's or agent's file reference <b>P. IMEC .85B/WO</b>	<b>FOR FURTHER ACTION</b> See paragraphs 1 and 4 below
International application No. <b>PCT/BE 98/ 00159</b>	International filing date <i>(day, month, year)</i> <div style="text-align: right; font-weight: bold;">22/10/1998</div>
Applicant  <b>INTERUNIVERSITAIR MICRO-ELEKTRONICA CENTRUM et al.</b>	

1. ☒ The applicant is hereby notified that the International Search Report has been established and is transmitted herewith.

**Filing of amendments and statement under Article 19**

The applicant is entitled, if he so wishes, to amend the claims of the International Application (see Rule 46):

**When?** The time limit for filing such amendments is normally 2 months from the date of transmittal of the International Search Report; however, for more details, see the notes on the accompanying sheet.

**Where?** Directly to the      International Bureau of WIPO  
 34, chemin des Colombettes  
 1211 Geneva 20, Switzerland  
 Facsimile No.: (41-22) 740.14.35

**For more detailed instructions,** see the notes on the accompanying sheet.

2. ☐ The applicant is hereby notified that no International Search Report will be established and that the declaration under Article 17(2)(a) to that effect is transmitted herewith.

3. ☐ **With regard to the protest** against payment of (an) additional fee(s) under Rule 40.2, the applicant is notified that:

☐ the protest together with the decision thereon has been transmitted to the International Bureau together with the applicant's request to forward the texts of both the protest and the decision thereon to the designated Offices.

☐ no decision has been made yet on the protest; the applicant will be notified as soon as a decision is made.

4. **Further action(s):** The applicant is reminded of the following:

Shortly after **18 months** from the priority date, the international application will be published by the International Bureau. If the applicant wishes to avoid or postpone publication, a notice of withdrawal of the international application, or of the priority claim, must reach the International Bureau as provided in Rules 90bis 1 and 90bis 3, respectively, before the completion of the technical preparations for international publication.

Within **19 months** from the priority date, a demand for international preliminary examination must be filed if the applicant wishes to postpone the entry into the national phase until 30 months from the priority date (in some Offices even later).

Within **20 months** from the priority date, the applicant must perform the prescribed acts for entry into the national phase before all designated Offices which have not been elected in the demand or in a later election within 19 months from the priority date or could not be elected because they are not bound by Chapter II.

Name and mailing address of the International Searching Authority  European Patent Office, P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel. (+31-70) 340-2040. Tx 31 651 epo nl. Fax: (+31-70) 340-3016	Authorized officer  <b>Mark Quinn</b>
---	---



## NOTES TO FORM PCT/ISA/220

These Notes are intended to give the basic instructions concerning the filing of amendments under article 19. The Notes are based on the requirements of the Patent Cooperation Treaty, the Regulations and the Administrative Instructions under that Treaty. In case of discrepancy between these Notes and those requirements, the latter are applicable. For more detailed information, see also the PCT Applicant's Guide, a publication of WIPO.

In these Notes, "Article", "Rule", and "Section" refer to the provisions of the PCT, the PCT Regulations and the PCT Administrative Instructions respectively.

### INSTRUCTIONS CONCERNING AMENDMENTS UNDER ARTICLE 19

The applicant has, after having received the international search report, one opportunity to amend the claims of the international application. It should however be emphasized that, since all parts of the international application (claims, description and drawings) may be amended during the international preliminary examination procedure, there is usually no need to file amendments of the claims under Article 19 except where, e.g. the applicant wants the latter to be published for the purposes of provisional protection or has another reason for amending the claims before international publication. Furthermore, it should be emphasized that provisional protection is available in some States only.

#### What parts of the international application may be amended?

Under Article 19, only the claims may be amended.

During the international phase, the claims may also be amended (or further amended) under Article 34 before the International Preliminary Examining Authority. The description and drawings may only be amended under Article 34 before the International Examining Authority.

Upon entry into the national phase, all parts of the international application may be amended under Article 28 or, where applicable, Article 41.

#### When?

Within 2 months from the date of transmittal of the international search report or 16 months from the priority date, whichever time limit expires later. It should be noted, however, that the amendments will be considered as having been received on time if they are received by the International Bureau after the expiration of the applicable time limit but before the completion of the technical preparations for international publication (Rule 46.1).

#### Where not to file the amendments?

The amendments may only be filed with the International Bureau and not with the receiving Office or the International Searching Authority (Rule 46.2).

Where a demand for international preliminary examination has been/is filed, see below.

#### How?

Either by cancelling one or more entire claims, by adding one or more new claims or by amending the text of one or more of the claims as filed.

A replacement sheet must be submitted for each sheet of the claims which, on account of an amendment or amendments, differs from the sheet originally filed.

All the claims appearing on a replacement sheet must be numbered in Arabic numerals. Where a claim is cancelled, no renumbering of the other claims is required. In all cases where claims are renumbered, they must be renumbered consecutively (Administrative Instructions, Section 205(b)).

The amendments must be made in the language in which the international application is to be published.

#### What documents must/may accompany the amendments?

**Letter (Section 205(b)):**

The amendments must be submitted with a letter.

The letter will not be published with the international application and the amended claims. It should not be confused with the "Statement under Article 19(1)" (see below, under "Statement under Article 19(1)").

The letter must be in English or French, at the choice of the applicant. However, if the language of the international application is English, the letter must be in English; if the language of the international application is French, the letter must be in French.





## NOTES TO FORM PCT/ISA/220 (continued)

The letter must indicate the differences between the claims as filed and the claims as amended. It must, in particular, indicate, in connection with each claim appearing in the international application (it being understood that identical indications concerning several claims may be grouped), whether

- (i) the claim is unchanged,
- (ii) the claim is cancelled;
- (iii) the claim is new,
- (iv) the claim replaces one or more claims as filed,
- (v) the claim is the result of the division of a claim as filed

**The following examples illustrate the manner in which amendments must be explained in the accompanying letter:**

- 1 [Where originally there were 48 claims and after amendment of some claims there are 51]:  
"Claims 1 to 29, 31, 32, 34, 35, 37 to 48 replaced by amended claims bearing the same numbers, claims 30, 33 and 36 unchanged, new claims 49 to 51 added."
- 2 [Where originally there were 15 claims and after amendment of all claims there are 11]:  
"Claims 1 to 15 replaced by amended claims 1 to 11."
- 3 [Where originally there were 14 claims and the amendments consist in cancelling some claims and in adding new claims]:  
"Claims 1 to 6 and 14 unchanged, claims 7 to 13 cancelled; new claims 15, 16 and 17 added." or  
"Claims 7 to 13 cancelled; new claims 15, 16 and 17 added; all other claims unchanged."
- 4 [Where various kinds of amendments are made]:  
"Claims 1-10 unchanged; claims 11 to 13, 18 and 19 cancelled; claims 14, 15 and 16 replaced by amended claim 14, claim 17 subdivided into amended claims 15, 16 and 17; new claims 20 and 21 added."

### **"Statement under article 19(1)" (Rule 46.4)**

The amendments may be accompanied by a statement explaining the amendments and indicating any impact that such amendments might have on the description and the drawings (which cannot be amended under Article 19(1)).

The statement will be published with the international application and the amended claims.

**It must be in the language in which the international application is to be published.**

It must be brief, not exceeding 500 words if in English or if translated into English.

It should not be confused with and does not replace the letter indicating the differences between the claims as filed and as amended. It must be filed on a separate sheet and must be identified as such by a heading, preferably by using the words "Statement under Article 19(1)."

It may not contain any disparaging comments on the international search report or the relevance of citations contained in that report. Reference to citations, relevant to a given claim, contained in the international search report may be made only in connection with an amendment of that claim.

### **Consequence if a demand for international preliminary examination has already been filed**

If, at the time of filing any amendments under Article 19, a demand for international preliminary examination has already been submitted, the applicant must preferably, at the same time of filing the amendments with the International Bureau, also file a copy of such amendments with the International Preliminary Examining Authority (see Rule 62.2(a), first sentence).

### **Consequence with regard to translation of the international application for entry into the national phase**

The applicant's attention is drawn to the fact that, where upon entry into the national phase, a translation of the claims as amended under Article 19 may have to be furnished to the designated/elected Offices, instead of, or in addition to, the translation of the claims as filed.

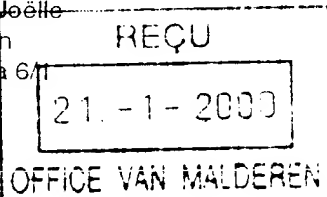
For further details on the requirements of each designated/elected Office, see Volume II of the PCT Applicant's Guide.



From the  
INTERNATIONAL PRELIMINARY EXAMINING AUTHORITY

To:

VAN MALDEREN, Joëlle  
Office Van Malderen  
Place Reine Fabiola 6/1  
B-1083 Brussels  
BELGIQUE



PCT

NOTIFICATION OF TRANSMITTAL OF  
THE INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT  
(PCT Rule 71.1)

Date of mailing  
(day/month/year) 19.01.2000

Applicant's or agent's file reference  
P.I MEC.85B/WO

**IMPORTANT NOTIFICATION**

International application No.  
PCT/BE98/00159

International filing date (day/month/year)  
22/10/1998

Priority date (day/month/year)  
22/10/1997

Applicant  
INTERUNIVERSITAIR MICRO-ELEKTRONICA CENTRUM et al.

1. The applicant is hereby notified that this International Preliminary Examining Authority transmits herewith the international preliminary examination report and its annexes, if any, established on the international application.
2. A copy of the report and its annexes, if any, is being transmitted to the International Bureau for communication to all the elected Offices.
3. Where required by any of the elected Offices, the International Bureau will prepare an English translation of the report (but not of any annexes) and will transmit such translation to those Offices.

**4. REMINDER**

The applicant must enter the national phase before each elected Office by performing certain acts (filing translations and paying national fees) within 30 months from the priority date (or later in some Offices) (Article 39(1)) (see also the reminder sent by the International Bureau with Form PCT/IB/301).

Where a translation of the international application must be furnished to an elected Office, that translation must contain a translation of any annexes to the international preliminary examination report. It is the applicant's responsibility to prepare and furnish such translation directly to each elected Office concerned.

For further details on the applicable time limits and requirements of the elected Offices, see Volume II of the PCT Applicant's Guide.

Name and mailing address of the IPEA:



European Patent Office  
D-80238 Munich  
Tel: +49 89 2399 - 0 Tx: 523656 epmu d  
Fax: +49 89 2399 - 4465

Authorized officer

Magliano, D

Tel +49 89 2399-2422





# PATENT COOPERATION TREATY

PCT

## NOTIFICATION CONCERNING SUBMISSION OR TRANSMITTAL OF PRIORITY DOCUMENT

(PCT Administrative Instructions, Section 411)

From the INTERNATIONAL BUREAU

To:

VAN MALDEREN, Joëlle  
Office Van Malderen  
Place Reine Fabiola 6/  
B-1083 Brussels  
BELGIQUE

RECEIVED  
- 1 - 3 - 1999

OFFICE VAN MALDEREN

Date of mailing (day/month/year) 22 February 1999 (22.02.99)	
Applicant's or agent's file reference P.IMEC.85B/WO	IMPORTANT NOTIFICATION
International application No. PCT/BE98/00159	International filing date (day/month/year) 22 October 1998 (22.10.98)
International publication date (day/month/year) Not yet published	Priority date (day/month/year) 22 October 1997 (22.10.97)
Applicant INTERUNIVERSITAIR MICRO-ELEKTRONICA CENTRUM et al	

- The applicant is hereby notified of the date of receipt (except where the letters "NR" appear in the right-hand column) by the International Bureau of the priority document(s) relating to the earlier application(s) indicated below. Unless otherwise indicated by an asterisk appearing next to a date of receipt, or by the letters "NR", in the right-hand column, the priority document concerned was submitted or transmitted to the International Bureau in compliance with Rule 17.1(a) or (b).
- This updates and replaces any previously issued notification concerning submission or transmittal of priority documents.
- An **asterisk(\*)** appearing next to a date of receipt, in the right-hand column, denotes a priority document submitted or transmitted to the International Bureau but not in compliance with Rule 17.1(a) or (b). In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.
- The **letters "NR"** appearing in the right-hand column denote a priority document which was not received by the International Bureau or which the applicant did not request the receiving Office to prepare and transmit to the International Bureau, as provided by Rule 17.1(a) or (b), respectively. In such a case, **the attention of the applicant is directed** to Rule 17.1(c) which provides that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity, upon entry into the national phase, to furnish the priority document within a time limit which is reasonable under the circumstances.

Priority date	Priority application No.	Country or regional Office or PCT receiving Office	Date of receipt of priority document
22 Octo 1997 (22.10.97)	60/063,487	US	14 Janu 1999 (14.01.99)
12 Febr 1998 (12.02.98)	60/074,524	US	14 Janu 1999 (14.01.99)
18 May 1998 (18.05.98)	98870111.6	EP	09 Febr 1999 (09.02.99)

The International Bureau of WIPO  
34, chemin des Colombettes  
1211 Geneva 20, Switzerland

Facsimile No. (41-22) 740.14.35

Authorized officer

F. Gateau

Telephone No. (41-22) 338.83.38



## PATENT COOPERATION TREATY

PCT

INFORMATION CONCERNING ELECTED  
OFFICES NOTIFIED OF THEIR ELECTION

(PCT Rule 61.3)

From the INTERNATIONAL BUREAU

To:

VAN MALDEREN, Joëlle  
Office Van Malderen  
Place Reine Fabiola 6/1  
B-1083 Brussels  
BELGIQUE

Date of mailing (day/month/year) 29 April 1999 (29.04.99)		
Applicant's or agent's file reference P.IMEC.85B/WO		IMPORTANT INFORMATION
International application No. PCT/BE98/00159	International filing date (day/month/year) 22 October 1998 (22.10.98)	Priority date (day/month/year) 22 October 1997 (22.10.97)
Applicant INTERUNIVERSITAIR MICRO-ELEKTRONICA CENTRUM et al		

1. The applicant is hereby informed that the International Bureau has, according to Article 31(7), notified each of the following Offices of its election:

EP : AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE  
National : JP, US

2. The following Offices have waived the requirement for the notification of their election: the notification will be sent to them by the International Bureau only upon their request:

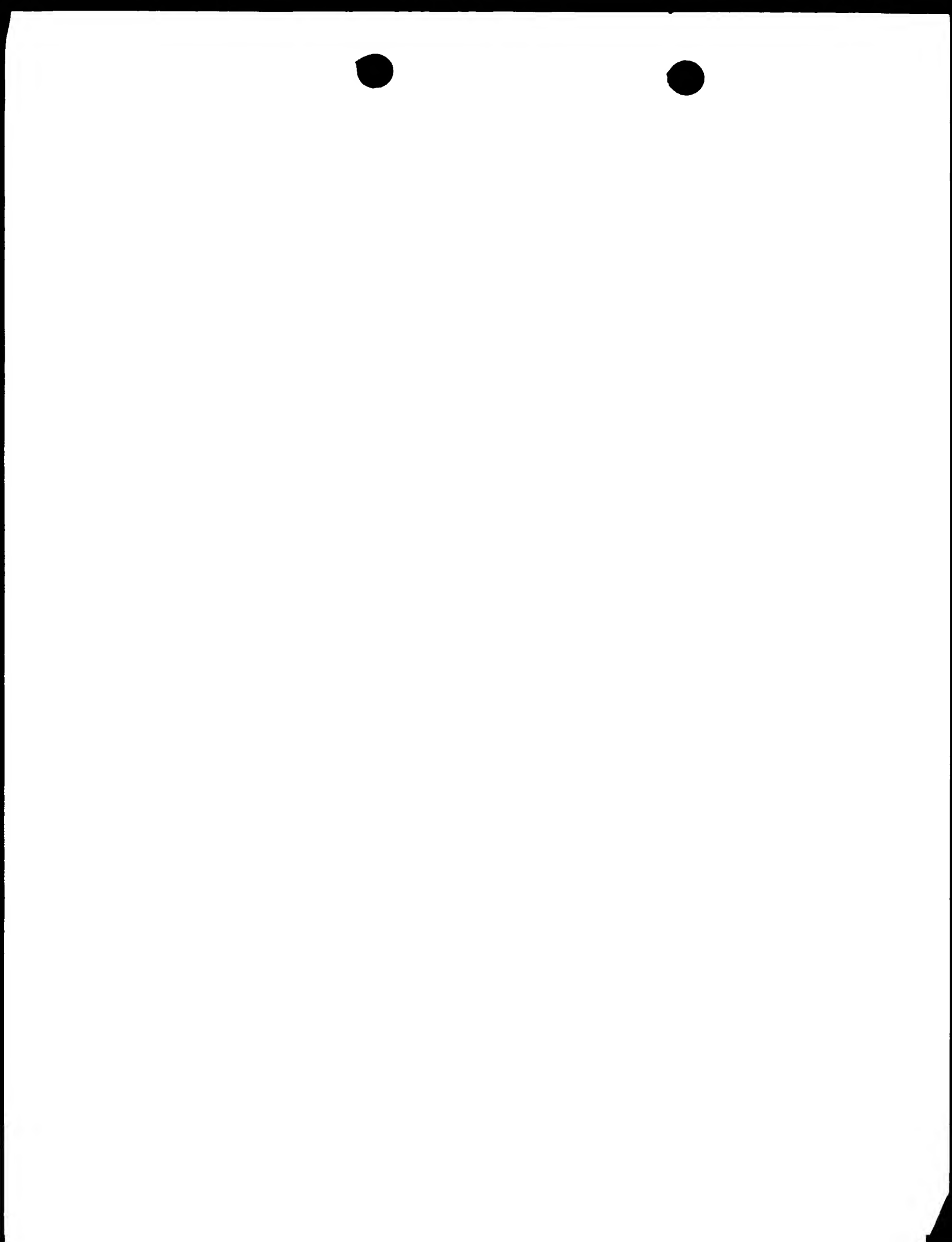
None

3. The applicant is reminded that he must enter the "national phase" **before the expiration of 30 months from the priority date** before each of the Offices listed above. This must be done by paying the national fee(s) and furnishing, if prescribed, a translation of the international application (Article 39(1)(a)), as well as, where applicable, by furnishing a translation of any annexes of the international preliminary examination report (Article 36(3)(b) and Rule 74.1).

Some offices have fixed time limits expiring later than the above-mentioned time limit. For detailed information about the applicable time limits and the acts to be performed upon entry into the national phase before a particular Office, see Volume II of the PCT Applicant's Guide.

The entry into the European regional phase is postponed until 31 months from the priority date for all States designated for the purposes of obtaining a European patent including, where applicable, ES which cannot be elected since it is not bound by Chapter II.

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland  Facsimile No. (41-22) 740.14.35	Authorized officer:  J. Zahra  Telephone No. (41-22) 338.83.38
--	--





RECD 24 JAN 2000

PCT

## INTERNATIONAL PRELIMINARY EXAMINATION REPORT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P.IMEC.85B/WO	<b>FOR FURTHER ACTION</b> See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416)	
International application No. PCT/BE98/00159	International filing date (day/month/year) 22/10/1998	Priority date (day/month/year) 22/10/1997
International Patent Classification (IPC) or national classification and IPC H01L21/3065		
Applicant INTERUNIVERSITAIR MICRO-ELEKTRONICA CENTRUM et al.		

1. This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.



2. This REPORT consists of a total of 6 sheets, including this cover sheet.

- ☒ This report is also accompanied by ANNEXES, i.e. sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 4 sheets.

3. This report contains indications relating to the following items:

- I ☒ Basis of the report
- II ☐ Priority
- III ☐ Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
- IV ☐ Lack of unity of invention
- V ☒ Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
- VI ☒ Certain documents cited
- VII ☐ Certain defects in the international application
- VIII ☒ Certain observations on the international application

Date of submission of the demand 03/03/1999	Date of completion of this report 19.01.2000
Name and mailing address of the international preliminary examining authority:  European Patent Office D-80298 Munich Tel. +49 89 2399 - 0 Tx: 523656 epmu d Fax: +49 89 2399 - 4465	Authorized officer Thiele, N Telephone No. +49 89 2399 2598 



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/BE98/00159

**I. Basis of the report**

1. This report has been drawn on the basis of (*substitute sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to the report since they do not contain amendments.*):

**Description, pages:**

1-17 as originally filed

**Claims, No.:**

1-16 as received on 26/10/1999 with letter of 21/10/1999

**Drawings, sheets:**

1/6-6/6 as originally filed

2. The amendments have resulted in the cancellation of:

- ☐ the description, pages:  
☒ the claims, Nos.: 17  
☐ the drawings, sheets:

3. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed (Rule 70.2(c)):

4. Additional observations, if necessary:



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT**

International application No. PCT/BE98/00159

**V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**

**1. Statement**

Novelty (N)	Yes:	Claims	1-8,10-16
	No:	Claims	9
Inventive step (IS)	Yes:	Claims	16
	No:	Claims	1-15
Industrial applicability (IA)	Yes:	Claims	1-16
	No:	Claims	

**2. Citations and explanations**

**see separate sheet**

**VI. Certain documents cited**

**1. Certain published documents (Rule 70.10)**

and / or

**2. Non-written disclosures (Rule 70.9)**

**see separate sheet**

**VIII. Certain observations on the international application**

The following observations on the clarity of the claims, description, and drawings or on the question whether the claims are fully supported by the description, are made:

**see separate sheet**



## **Chapter V**

The document cited in Chapter VI could affect novelty, if it was to be considered (it is at present doubtful, if the priority has been validly claimed).

1) See first chapter VIII.

2) Present claim 1 concerns a method being completely different from the method of claim 9 on file since the opening according to claim 9 is not fluorinated, it is not mentioned that an anisotropy should be achieved, and oxygen-containing gas is used instead of fluorine-containing gas. Since it appeared that the method of claim 9 is a further step to be carried out (as a preferred embodiment) after the step described in claim 1, an objection with regard to lack of unity was not raised; the Applicant took the opportunity to file a new claim 16 combining the subject-matter of claims 1 and 9, but still maintains claim 9. It therefore does not seem that claim 9 could remain in this application.

3) Notwithstanding this it is pointed to the following documents:

D1: US-A-3816196

D2: US-A-5176790

D3: US-A-4661204

D4: US-A-5173442

D5: US-A-5358902

4) D1 to D5 (see particularly the passages cited in the International Search Report) describe the formation of an opening in an insulating layer consisting of organic material in a reaction chamber using a gas mixture comprising a fluorine-containing (D1 to D3) or oxygen-containing (D4, D5) gas, whereby fluorinated sidewalls may result in the case of the use of a fluorine-containing gas, and anisotropic etching takes place. Since further gases are also present in the gas mixtures of the prior art, the expression "inert gas" in claim 1 (or claim 9) cannot be





considered to be a distinguishing feature without defining exactly gases useful for this purpose.

5) D4 discloses a hard mask and an additional resist layer on this hard mask, which is patterned (see e.g. figures 1a-1f and column 3, lines 44-57), and the etching gas contains a fluorine-containing gas and at least one further gas. The disclaimer introduced into claim 1 can be considered to establish novelty formally, although D4 does not exclude oxygen-free plasmas. Nevertheless a disclaimer may make an accidentally overlapping teaching novel, but cannot make an obvious teaching inventive. Thus, claim 1 cannot be considered to involve an inventive step.

D4 also discloses the application of an oxygen-containing gas. Therefore claim 9 lacks novelty.

The subject-matter of claims 2 to 8 and 10 to 15 appears to be conventional.

6) Claim 16 on file can be considered to be distinguished from the cited prior art documents, and also seems to involve an inventive step. cannot be denied.

7) The industrial applicability cannot be denied.

## **Chapter VI**

JP-A-10012617 (abstract) Priority 26.06.96; published 16.01.98

## **Chapter VIII**

1) The description is not in conformity with the new set of claims.

2) Claim 1 appears to be unclear, because no technical feature is indicated how the plasma etching must be controlled in order to achieve the desired result, i.e. no deposition of etch residues. Claim 10 is unclear since no information is given how to choose the ratio to avoid spontaneous etching. The Applicant contested that it was necessary to



**INTERNATIONAL PRELIMINARY  
EXAMINATION REPORT - SEPARATE SHEET**

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International application No. PCT/BE98/00159

specify how the desired results can be achieved and stated in his letter that the selection of those conditions would be obvious for a skilled person, i.e. an invention definitely could not be seen in the solution how to achieve these desired results.



5

CLAIMS

1. A method for forming at least one opening  
in an organic-containing insulating layer, comprising the  
10 steps of:

covering said organic-containing insulating  
layer with a bilayer, said bilayer comprising a resist hard  
mask layer, being formed on said organic-containing  
insulating layer, and a resist layer being formed on said  
15 resist hard mask layer,

patterning said bilayer,  
creating said opening by plasma etching said insulating  
layer in a reaction chamber containing a gaseous mixture,  
said gaseous mixture comprising a fluorine-containing gas,  
20 an inert gas and essentially not an oxygen-containing gas;  
and

controlling said plasma etching, while  
creating said opening, in a manner that substantially no  
etch residues are deposited and that the side walls of said  
25 opening are fluorinated during said plasma etching to  
thereby enhance the anisotropy of said plasma etching.

2. A method as recited in claim 1, wherein  
said organic-containing insulating layer comprises at least  
one unsaturated carbon bond.

30 3. A method as recited in claim 2, wherein  
said organic-containing insulating layer is selected from a  
group comprising the benzocyclobutarenes, poly arylene  
ether, aromatic hydrocarbon and polyamides.

4. A method as recited in claim 1, wherein

AMENDED SHEET



said resist hard mask layer is a silicon oxide, or a silicon nitride, or a silicon oxynitride, or a silicon carbide, or a silicon oxycarbide layer.

5 A method as recited in claim 1, wherein said inert gas is nitrogen and wherein the ratio of the amount of nitrogen in said gaseous mixture to the amount of fluorine containing gas in said gaseous mixture is larger than 2:1.

10 6. A method as recited in claim 1, wherein said fluorine-containing gas is  $\text{SF}_6$ , or  $\text{NF}_3$ , or  $\text{C}_2\text{F}_6$ , or  $\text{CF}_4$  or  $\text{CHF}_3$  or  $\text{CH}_3\text{F}$  or  $\text{CH}_2\text{F}_2$  or mixtures thereof.

15 7. A method as recited in claim 1, wherein said opening is at least one via hole, said via hole extending through said insulating layer to an underlying conductive layer or an underlying barrier layer.

8. A method as recited in claim 1, wherein said gaseous mixture further comprises an oxygen containing gas.

20 9. A method for forming at least one opening in an organic-containing insulating layer comprising the step of:

covering said organic-containing insulating layer with a bilayer, said bilayer comprising a resist hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said resist hard mask layer,

patterning said bilayer,

30 creating said opening by plasma etching said organic-containing insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising an oxygen-containing gas and an inert gas, said inert gas and said oxygen-containing gas being present in said gaseous mixture at a predetermined ratio, said ratio being chosen such that spontaneous etching is substantially





avoided.

10. A method as recited in claim 9, wherein said organic-containing insulating layer is a low K organic polymer layer.

5 11. A method as recited in claim 9, wherein said resist layer is selectively removed from said hard mask layer while creating said opening.

12. A method as recited in claim 9, wherein said oxygen-containing gas in said gaseous mixture is O<sub>2</sub>  
10 and said inert gas in said gaseous mixture is nitrogen.

13. A method as recited in claim 12, wherein said ratio of nitrogen in said gaseous mixture to oxygen in said gaseous mixture is in the range from 5:1 to 2:1.

14. A method as recited in claim 10, wherein  
15 prior to plasma etching in said reaction chamber containing said gaseous mixture, a first part of said opening is created by plasma etching said insulating layer in said reaction chamber containing a first gaseous mixture, said first gaseous mixture comprising a fluorine-containing gas  
20 and an inert gas;

controlling said plasma etching in said reaction chamber containing said first gaseous mixture, while creating said first part of said opening, in a manner that substantially no etch residues are deposited and that  
25 the side walls of said first part of said opening are fluorinated during said plasma etching to thereby enhance the anisotropy of said plasma etching in said reaction chamber containing said first gaseous mixture.

15. A method as recited in claim 14, wherein  
30 said opening has positively sloped side walls.

16. A method for forming at least one opening in an organic-containing insulating layer, comprising the steps of:

covering said organic-containing insulating



layer with a bilayer, said bilayer comprising a resist hard mask layer, being formed on said organic-containing insulating layer, and a resist layer being formed on said resist hard mask layer,

5                   patterning said bilayer,

                  creating said first part in said opening by plasma etching said insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising a fluorine-containing gas, an inert gas and  
10 essentially not an oxygen-containing gas; and

                  controlling said plasma etching, while creating said first part in said opening, in a manner that the side walls of said first part of said opening are fluorinated during said plasma etching to thereby enhance  
15 the anisotropy of said plasma etching.

                  creating said second part in said opening by plasma etching said organic-containing insulating layer in a reaction chamber containing a gaseous mixture, said gaseous mixture comprising an oxygen-containing gas and an  
20 inert gas, said inert gas and said oxygen-containing gas being present in said gaseous mixture at a predetermined ratio, said ratio being chosen such that spontaneous etching is substantially avoided and being chosen such that said opening is completely formed whereby said resist layer  
25 is removed.



## INTERNATIONAL SEARCH REPORT

(PCT Article 18 and Rules 43 and 44)

Applicant's or agent's file reference <b>P. IMEC.85B/WO</b>	<b>FOR FURTHER ACTION</b> see Notification of Transmittal of International Search Report (Form PCT/ISA/220) as well as, where applicable, item 5 below.	
International application No. <b>PCT/BE 98/ 00159</b>	International filing date (day/month/year) <b>22/10/1998</b>	(Earliest) Priority Date (day/month/year) <b>22/10/1997</b>
Applicant <b>INTERUNIVERSITAIR MICRO-ELEKTRONICA CENTRUM et al.</b>		

This International Search Report has been prepared by this International Searching Authority and is transmitted to the applicant according to Article 18. A copy is being transmitted to the International Bureau.

This International Search Report consists of a total of 3 sheets.

☒ It is also accompanied by a copy of each prior art document cited in this report.

1. ☐ **Certain claims were found unsearchable** (see Box I).
2. ☐ **Unity of invention is lacking** (see Box II).
3. ☐ The international application contains disclosure of a **nucleotide and/or amino acid sequence listing** and the international search was carried out on the basis of the sequence listing
  - ☐ filed with the international application.
  - ☐ furnished by the applicant separately from the international application.
    - ☐ but not accompanied by a statement to the effect that it did not include matter going beyond the disclosure in the international application as filed.
  - ☐ Transcribed by this Authority
4. With regard to the **title**, ☒ the text is approved as submitted by the applicant  
☐ the text has been established by this Authority to read as follows:
5. With regard to the **abstract**, ☒ the text is approved as submitted by the applicant  
☐ the text has been established, according to Rule 38.2(b), by this Authority as it appears in Box III. The applicant may, within one month from the date of mailing of this international Search Report, submit comments to this Authority.
6. The figure of the **drawings** to be published with the abstract is:
  - Figure No.      ☐ as suggested by the applicant.
  - ☐ because the applicant failed to suggest a figure.
  - ☐ because this figure better characterizes the invention.
  - ☒ None of the figures.



## INTERNATIONAL SEARCH REPORT

International Application No

P 98/00159

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 H01L21/3065

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	US 3 816 196 A (LA COMBE) 11 June 1974 see Abstract see claims 1,2 ---	1-15
X,P	PATENT ABSTRACTS OF JAPAN vol. 98, no. 5, 30 April 1998 & JP 10 012617 A (MITSUBISHI ELECTRIC CORP.), 16 January 1998 see Abstract ---	1-15
X	US 5 176 790 A (ARLEO ET AL.) 5 January 1993 cited in the application see claims 1,2,17,26; figures 1,2 --- -/--	1-9



Further documents are listed in the continuation of box C



Patent family members are listed in annex

**Special categories of cited documents:**

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

&amp; document member of the same patent family

Date of the actual completion of the international search

12 February 1999

Date of mailing of the international search report

03/03/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx 31 651 epo nl.  
Fax: (+31-70) 340-3016

Authorized officer

Thiele, N





## INTERNATIONAL SEARCH REPORT

International Application No

BF 98/00159

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication where appropriate, of the relevant passages	Relevant to claim No
X	US 4 661 204 A (MATHUR ET AL.) 28 April 1987 see Abstract see claims 1,4-6 ---	1-15
X	US 5 173 442 A (CAREY) 22 December 1992 see column 4, line 3-8; claim 1; figures 1A-1F ---	1-15
X	US 5 358 902 A (VERHAAR ET AL.) 25 October 1994 see column 5, line 22-32 see claims 1,2,7 ---	1-15
A	DATABASE WPI Section Ch, Week 9530 Derwent Publications Ltd., London, GB: Class L03, AN 95-230257 XP002093190 & RU 2 024 991 A (MOLECULAR ELECTRON RES. INST.), 15 December 1994 see abstract ---	1-17
A	US 5 269 879 A (RHOADES ET AL. ) 14 December 1993 cited in the application see Abstract ---	1-17
A	EP 0 127 188 A (KK TOSHIBA) 5 December 1994 see claims 9-14 -----	1-17



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

EP 98/00159

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 3816196	A	11-06-1974	NONE	
US 5176790	A	05-01-1993	NONE	
US 4661204	A	28-04-1987	AU 581110 B	09-02-1989
			AU 6549886 A	19-05-1987
			EP 0244462 A	11-11-1987
			JP 63501186 T	28-04-1988
			WO 8702626 A	07-05-1987
US 5173442	A	22-12-1992	US 5091339 A	25-02-1992
			US 5219787 A	15-06-1993
US 5358902	A	25-10-1994	GB 2233494 A	09-01-1991
			DE 69018884 D	01-06-1995
			DE 69018884 T	07-12-1995
			EP 0405660 A	02-01-1991
			JP 2776960 B	16-07-1998
			JP 3034539 A	14-02-1991
US 5269879	A	14-12-1993	US 5658425 A	19-08-1997
EP 127188	A	05-12-1984	JP 1895081 C	26-12-1994
			JP 6022212 B	23-03-1994
			JP 59220925 A	12-12-1984
			US 4529475 A	16-07-1985



# PATENT COOPERATION TREATY

PCT

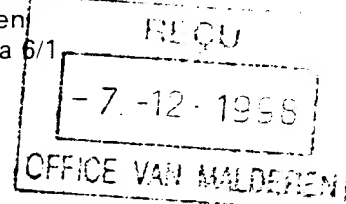
From the INTERNATIONAL BUREAU

## NOTIFICATION OF RECEIPT OF RECORD COPY

(PCT Rule 24.2(a))

To:

VAN MALDEREN, Joëlle  
Office Van Malderen  
Place Reine Fabiola 6/1  
B-1083 Brussels  
BELGIQUE



<b>Date of mailing</b> (day/month/year) 19 November 1998 (19.11.98)	<b>IMPORTANT NOTIFICATION</b>
<b>Applicant's or agent's file reference</b> P.IMEC.85B/WO	<b>International application No.</b> PCT/BE98/00159

The applicant is hereby notified that the International Bureau has received the record copy of the international application as detailed below.

Name(s) of the applicant(s) and State(s) for which they are applicants:

INTERUNIVERSITAIR MICRO-ELEKTRONICA CENTRUM (for all designated States except US)

VANHAELEMEERSCH, Serge et al (for US)

International filing date : 22 October 1998 (22.10.98)  
Priority date(s) claimed : 22 October 1997 (22.10.97)  
12 February 1998 (12.02.98)  
18 May 1998 (18.05.98)  
Date of receipt of the record copy by the International Bureau : 18 November 1998 (18.11.98)  
List of designated Offices :

EP : AT,BE,CH,CY,DE,DK,ES,FI,FR,GB,GR,IE,IT,LU,MC,NL,PT,SE  
National : JP,US

### ATTENTION

The applicant should carefully check the data appearing in this Notification. In case of any discrepancy between these data and the indications in the international application, the applicant should immediately inform the International Bureau.

In addition, the applicant's attention is drawn to the information contained in the Annex, relating to:

- ☒ time limits for entry into the national phase
- ☒ confirmation of precautionary designations
- ☒ requirements regarding priority documents

A copy of this Notification is being sent to the receiving Office and to the International Searching Authority.

<b>The International Bureau of WIPO</b> 34, chemin des Colombettes 1211 Geneva 20, Switzerland	<b>Authorized officer:</b>  F. Gateau  Telephone No. (41-22) 338.83.38
Facsimile No. (41-22) 740.14.35	



## INFORMATION ON TIME LIMITS FOR ENTERING THE NATIONAL PHASE

The applicant is reminded that the "national phase" must be entered before each of the designated Offices indicated in the Notification of Receipt of Record Copy (Form PCT/IB/301) by paying national fees and furnishing translations, as prescribed by the applicable national laws.

The time limit for performing these procedural acts is **20 MONTHS** from the priority date or, for those designated States which the applicant elects in a demand for international preliminary examination or in a later election, **30 MONTHS** from the priority date, provided that the election is made before the expiration of 19 months from the priority date. Some designated (or elected) Offices have fixed time limits which expire even later than 20 or 30 months from the priority date. In other Offices an extension of time or grace period, in some cases upon payment of an additional fee, is available.

In addition to these procedural acts, the applicant may also have to comply with other special requirements applicable in certain Offices. **It is the applicant's responsibility** to ensure that the necessary steps to enter the national phase are taken in a timely fashion. Most designated Offices do not issue reminders to applicants in connection with the entry into the national phase.

**For detailed information about the procedural acts to be performed to enter the national phase before each designated Office, the applicable time limits and possible extensions of time or grace periods, and any other requirements, see the relevant Chapters of Volume II of the PCT Applicant's Guide. Information about the requirements for filing a demand for international preliminary examination is set out in Chapter IX of Volume I of the PCT Applicant's Guide.**

GR and ES became bound by PCT Chapter II on 7 September 1996 and 6 September 1997, respectively, and may, therefore, be elected in a demand or a later election filed on or after 7 September 1996 and 6 September 1997, respectively, regardless of the filing date of the international application. (See second paragraph above.)

Note that only an applicant who is a national or resident of a PCT Contracting State which is bound by Chapter II has the right to file a demand for international preliminary examination.

## CONFIRMATION OF PRECAUTIONARY DESIGNATIONS

This notification lists only specific designations made under Rule 4.9(a) in the request. It is important to check that these designations are correct. Errors in designations can be corrected where precautionary designations have been made under Rule 4.9(b). The applicant is hereby reminded that any precautionary designations may be confirmed according to Rule 4.9(c) before the expiration of 15 months from the priority date. If it is not confirmed, it will automatically be regarded as withdrawn by the applicant. There will be no reminder and no invitation. Confirmation of a designation consists of the filing of a notice specifying the designated State concerned (with an indication of the kind of protection or treatment desired) and the payment of the designation and confirmation fees. Confirmation must reach the receiving Office within the 15-month time limit.

## REQUIREMENTS REGARDING PRIORITY DOCUMENTS

For applicants who have not yet complied with the requirements regarding priority documents, the following is recalled.

Where the priority of an earlier national, regional or international application is claimed, the applicant must submit a copy of the said earlier application, certified by the authority with which it was filed ("the priority document") to the receiving Office (which will transmit it to the International Bureau) or directly to the International Bureau, before the expiration of 16 months from the priority date, provided that any such priority document may still be submitted to the International Bureau before that date of international publication of the international application, in which case that document will be considered to have been received by the International Bureau on the last day of the 16-month time limit (Rule 17.1(a)).

Where the priority document is issued by the receiving Office, the applicant may, instead of submitting the priority document, request the receiving Office to prepare and transmit the priority document to the International Bureau. Such request must be made before the expiration of the 16-month time limit and may be subjected by the receiving Office to the payment of a fee (Rule 17.1(b)).

If the priority document concerned is not submitted to the International Bureau or if the request to the receiving Office to prepare and transmit the priority document has not been made (and the corresponding fee, if any, paid) within the applicable time limit indicated under the preceding paragraphs, any designated State may disregard the priority claim, provided that no designated Office may disregard the priority claim concerned before giving the applicant an opportunity to furnish the priority document within a time limit which is reasonable under the circumstances.

Where several priorities are claimed, the priority date to be considered for the purposes of computing the 16-month time limit is the filing date of the earliest application whose priority is claimed.

